SANDIA REPORT
SAND2022-6360
Printed April 2022
Unclassified Unlimited Release

Sandia National Laboratories

Calibrating the SPECTACULAR constitutive model using legacy Sandia data for two filled epoxy systems: 828/CTBN/DEA/GMB and 828/DEA/GMB

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ABSTRACT

The SPECTACULAR model is a development extension of the Simplified Potential Energy Clock (SPEC) model. Both models are nonlinear viscoelastic constitutive models used to predict a wide range of time-dependent behaviors in epoxies and other glass-forming materials. This report documents the procedures used to generate SPECTACULAR calibrations for two particulate-filled epoxy systems, 828/CTBN/DEA/GMB and 828/DEA/GMB. No previous SPECTACULAR or SPEC calibration exists for 828/CTBN/DEA/GMB, while a legacy SPEC calibration exists for 828/DEA/GMB. To generate the SPECTACULAR calibrations, a step-by-step procedure was executed to determine parameters in groups with minimal coupling between parameter groups. This procedure has often been deployed to calibrate SPEC, therefore the resulting SPECTACULAR calibration is backwards compatible with SPEC (i.e. none of the extensions specific to SPECTACULAR are used). The calibration procedure used legacy Sandia experimental data stored on the Polymer Properties Database website [2]. The experiments used for calibration included shear master curves, isofrequency temperature sweeps under oscillatory shear, the bulk modulus at room temperature, the thermal strain during a temperature sweep, and compression through yield at multiple temperatures below the glass transition temperature.

Overall, the calibrated models fit the experimental data remarkably well. However, the glassy shear modulus varies depending on the experiment used to calibrate it. For instance, the shear master curve, isofrequency temperature sweep under oscillatory shear, and the Young's modulus in glassy compression yield values for the glassy shear modulus at the reference temperature that vary by as much as 15 %. Also, for 828/CTBN/DEA/GMB, the temperature dependence of the glassy shear modulus when fit to the Young's modulus at different temperatures is approximately four times larger than when it is determined from the isofrequency temperature sweep under oscillatory shear. For 828/DEA/GMB, the temperature dependence of the shear modulus determined from the isofrequency temperature sweep under oscillatory shear accurately predicts the Young's modulus at different temperatures. When choosing values for the shear modulus, fitting the glassy compression data was prioritized. The new and legacy calibrations for 828/DEA/GMB are similar and appear to have been calibrated from the same data. However, the new calibration improves the fit to the thermal strain data.

In addition to the standard calibrations, development calibrations were produced that take advantage of development features of SPECTACULAR, including an updated equilibrium Helmholtz free energy that eliminates undesirable behavior found in previous work. In addition to the previously mentioned experimental data, the development calibrations require data for the heat capacity during a stress-free temperature sweep to calibrate thermal terms.

ACKNOWLEDGMENTS

The author would like to thank Benjamin Mann and Brenton Elisberg for reviewing this document. Their feedback improved the quality and clarity of this report.

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EXECUTIVE SUMMARY

- SPECTACULAR, a nonlinear viscoelastic constitutive model, was calibrated for two filled epoxy systems, 828/CTBN/DEA/GMB and 828/DEA/GMB. This document thoroughly describes the step-by-step calibration procedure.
- For both epoxies, the model was calibrated using legacy experimental data stored on the Polymer Properties Database website [2]. The data includes the shear master curve, storage shear modulus under an isofrequency temperature sweep, the bulk modulus at room temperature, the coefficient of thermal expansion during a stress-free temperature sweep, and uniaxial compression at temperatures below the glass transition temperature.
- The calibrated SPECTACULAR parameters for 828/CTBN/DEA/GMB are listed in Table 4-11. Model predictions are compared to experimental data in Fig. 4-7. The complete material definition for use with Sierra/SM is written in Appendix A.
- The calibrated SPECTACULAR parameters for 828/DEA/GMB are listed in Table 4-11. Model predictions are compared to experimental data in Fig. 4-8. The complete material definition for use with Sierra/SM is written in Appendix B.
- Overall, the model predictions agree satisfactorily with experiments. However, two broad conflicts required prioritizing one subset of experiments over another.
  - First, the shear master curve, storage modulus under an isofrequency temperature sweep, and glassy uniaxial compression provide conflicting values for the shear modulus. The different methods give values for the reference glassy modulus (G_g^{ref}) that vary by as much as 15 %. For 828/CTBN/DEA/GMB the temperature dependence of the glassy modulus (G_g') determined by the isofrequency temperature sweep ($G_g' = -2\,\text{MPa/K}$) is drastically different than the value determined from glassy compression at different temperatures ($G_g' = -9.2\,\text{MPa/K}$). When conflicts arose, the glassy compression data was prioritized.
  - Second, the model is unable to match the coefficient of thermal expansion during both heating and cooling. Fitting the coefficient of thermal expansion while cooling from an annealed state was prioritized. The heating fit is still reasonable, but the glass transition predicted by the model during heating is approximately 5 °C lower than in the experiments.
- The SPECTACULAR calibration for 828/DEA/GMB is compared to a previous calibration from SAND2011-4751 [1]. The parameters for the legacy calibration are listed in Table 4-11 and the model predictions are compared to experiments in Fig. 4-9. With a few exceptions, the parameters from the current and legacy calibrations are similar. The thermal strain relaxation function is narrower in the new calibration, which results in a better fit to

the coefficient of thermal expansion during a temperature sweep. The legacy calibration was converted from a SPEC [3] calibration into a SPECTACULAR calibration. The Sierra/SM material definition for the SPECTACULAR conversion of the legacy calibration is written in Appendix C.

- The use of legacy data creates a minor credibility issue for the new calibrations. Few details regarding experimental procedures are provided on the Polymer Properties Database website [2]. For viscoelasticity, the material behavior is history-dependent, so knowledge of experimental procedures is of particular importance. Where procedures were unknown, they were assumed to be the same as in Ref. [4], which also documents work on filled epoxies by D.B. Adolf. Since the new and legacy parameters for 828/DEA/GMB are similar, the assumptions about the experimental procedures appear reasonable, but they are assumptions nonetheless and should be indicated as such.
- The end of the report documents alternative model calibrations for 828/CTBN/DEA/GMB and 828/DEA/GMB that use development features of SPECTACULAR. These alternative calibrations are referred to as "development calibrations". The new features (1) allow for full thermomechanical coupling, (2) allow for the placement of the thermal relaxation function into the material clock (instead of the thermal strain relaxation function), and (3) modify the equilibrium Helmholtz free energy to eliminate undesirable model behavior regarding heat capacity calculations found in previous work [5].
- The parameters for the development calibrations are listed in Table 5-8 and model predictions are compared to experiments in Fig. 5-4 for 828/CTBN/DEA/GMB and Fig. 5-5 for 828/DEA/GMB. Material definitions for the development calibrations suitable for use with Sierra/SM are written in Appendix D and E for 828/CTBN/DEA/GMB and 828/DEA/GMB, respectively. These calibrations will not work as intended as of LAMÉ 5.4 [6]. Check the most recent SPECTACULAR documentation before deploying the development calibrations.

1. INTRODUCTION

This document describes in detail the procedure used to calibrate the nonlinear viscoelastic SPECTACULAR constitutive model for two epoxies filled with glass micro-balloons (GMB): 828/CTBN/DEA/GMB and 828/DEA/GMB. To my knowledge, no previous SPECTACULAR calibration exists for 828/CTBN/DEA/GMB. For 828/DEA/GMB, a previous model calibration exists [1], but details regarding the calibration procedure are sparse. Strictly speaking, the SPECTACULAR model theory was developed for unfilled epoxies. However, a study deploying the Potential Energy Clock (PEC) model [7, 8], a predecessor of SPECTACULAR, determined that filled epoxies could be treated as homogeneous continua and modeled using the formalism developed for neat epoxies [4]. Of course, treating the filled epoxy as homogeneous is only valid provided that damage mechanisms, such as matrix-particle debonding or crush, are inactive [9].

The document is organized as follows. The SPECTACULAR model equations are presented in Chapter 2. The experimental data used to characterize the materials is described in Chapter 3. Chapter 4 describes the calibration procedure for both materials, lists the calibrated parameters, and compares the current 828/DEA/GMB calibration to the previous calibration. Modified calibrations using development features of SPECTACULAR are presented in Chapter 5. A traditional conclusion is forgone in favor of an executive summary at the head of the memo.

2. MODEL FORMULATION

The SPECTACULAR model is nonlinear viscoelastic constitutive model that extends the Simplified Potential Energy Clock (SPEC) model [3]. The equations for SPECTACULAR are documented in Ref. [5] and its equations are derived starting from a Helmholtz free energy in Ref. [10]. There are two main differences between SPECTACULAR and SPEC. First, recent development on SPECTACULAR added equations for thermomechanical coupling [10], while SPEC only calculates the stress. Second, SPECTACULAR permits four separate relaxation functions, one for each of (1) volumetric, (2) shear, (3) thermal-volumetric (i.e. thermal strains), and (4) thermal relaxations, while SPEC allows for only two relaxation functions, (1) the volumetric and thermal-volumetric and (2) shear. Since SPEC does not include thermomechanical coupling, it does not use a purely thermal relaxation function. Both SPECTACULAR and SPEC are implemented within the Library of Advanced Materials for Engineering (LAMÉ) [6] for use in the Sierra/Solid Mechanics (Sierra/SM) finite element code [11]. SPEC is available in Sierra/SM as `universal_polymer` and SPECTACULAR is available as `spectacular`.

The equations for SPECTACULAR are given in this chapter to provide context for the parameters determined from the calibration procedure. The calibration procedure deployed in Chapter 4 follows a historical approach compatible with SPEC; only two independent relaxation functions are used and thermal calculations are ignored. To this end, only equations related to the calculation of the stress are presented here and equations related to thermal calculations are delayed until Chapter 5, where a calibration procedure is shown that utilizes development features of SPECTACULAR.

The SPECTACULAR constitutive response depends on the full strain and temperature histories of the material. The history is tracked through a hereditary integral formulation where relaxation functions are placed in convolution integrals with histories of the state variables. The Cauchy stress is written as

$$\begin{aligned}\boldsymbol{\sigma}(t) = &\left[K_g(\theta) - K_\infty(\theta)\right]\mathbf{1}\int_0^t f_1(t^*-s^*)\frac{\mathrm{d}I_1}{\mathrm{d}s}\mathrm{d}s \\ &-\left[K_g(\theta)\,\delta_g(\theta) - K_\infty(\theta)\,\delta_\infty(\theta)\right]\mathbf{1}\int_0^t f_3(t^*-s^*)\frac{\mathrm{d}\theta}{\mathrm{d}s}\mathrm{d}s \\ &+2\left[G_g(\theta) - G_\infty(\theta)\right]\int_0^t f_2(t^*-s^*)\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}s}\mathrm{d}s \\ &+\left[K_\infty(\theta)\,I_1 - K_\infty(\theta)\,\delta_\infty(\theta)\,(\theta-\theta_{\mathrm{sf}})\right]\mathbf{1} + 2G_\infty(\theta)\,\boldsymbol{e}.\end{aligned} \tag{2.1}$$

The symbol $\mathbf{1}$ is the second-order identity tensor, t is the current time, θ is the temperature, θ_{sf} is the stress-free temperature, and I_1 and $\boldsymbol{e}$ represent the first invariant and deviatoric tensor of the strain, $\boldsymbol{\varepsilon}$;

$$I_1 = \mathrm{tr}\,\boldsymbol{\varepsilon}, \qquad \boldsymbol{e} = \boldsymbol{\varepsilon} - \frac{I_1}{3}\mathbf{1}. \tag{2.2}$$

The temperature dependent bulk modulus, shear modulus, and (secant) volumetric coefficient of thermal expansion (CTE) are represented by K, G, and δ, while subscripts g and ∞ denote glassy (instantaneous) and rubbery (equilibrium) limits for those properties. These limiting properties are parameterized to depend linearly on temperature;

$$K_g(\theta) = K_g^{\text{ref}} + K_g'(\theta - \theta_{\text{ref}}), \qquad K_\infty(\theta) = K_\infty^{\text{ref}} + K_\infty'(\theta - \theta_{\text{ref}}), \tag{2.3}$$

$$G_g(\theta) = G_g^{\text{ref}} + G_g'(\theta - \theta_{\text{ref}}), \qquad G_\infty(\theta) = G_\infty^{\text{ref}} + G_\infty'(\theta - \theta_{\text{ref}}), \tag{2.4}$$

$$\delta_g(\theta) = \delta_g^{\text{ref}} + \delta_g'(\theta - \theta_{\text{ref}}), \qquad \delta_\infty(\theta) = \delta_\infty^{\text{ref}} + \delta_\infty'(\theta - \theta_{\text{ref}}). \tag{2.5}$$

Therefore, there are 6 functions associated with limiting properties, each defined by 2 parameters for a total of 12 parameters. The parameters for K and G are input directly to the model, but the parameters for δ are not model inputs. Instead, the user specifies the instantaneous CTE, α. To clarify the difference, δ and α are defined as

$$\delta(\theta) \coloneqq \frac{I_1}{\theta - \theta_{\text{sf}}}, \qquad \alpha(\theta) \coloneqq \frac{\mathrm{d}I_1}{\mathrm{d}\theta}. \tag{2.6}$$

The instantaneous CTE is also parameterized with a linear temperature dependence;

$$\alpha_g(\theta) = \alpha_g^{\text{ref}} + \alpha_g'(\theta - \theta_{\text{ref}}), \qquad \alpha_\infty(\theta) = \alpha_\infty^{\text{ref}} + \alpha_\infty'(\theta - \theta_{\text{ref}}). \tag{2.7}$$

The relationship between α and δ is easily found by integrating the volume strain from θ_{sf} to an arbitrary temperature θ under free expansion. The parameters for δ in terms of the parameters for α (the user inputs) are

$$\delta_g^{\text{ref}} = \alpha_g^{\text{ref}} + \frac{1}{2}\alpha_g'(\theta_{\text{sf}} - \theta_{\text{ref}}), \qquad \delta_\infty^{\text{ref}} = \alpha_\infty^{\text{ref}} + \frac{1}{2}\alpha_\infty'(\theta_{\text{sf}} - \theta_{\text{ref}}), \tag{2.8}$$

$$\delta_g' = \frac{1}{2}\alpha_g', \qquad \delta_\infty' = \frac{1}{2}\alpha_\infty'. \tag{2.9}$$

Three relaxation functions appear in the convolution integrals of Eq. (2.1): $f_1(x)$ is the volumetric relaxation function, $f_2(x)$ is the shear relaxation function, and $f_3(x)$ is the thermal-volumetric (i.e. thermal strain) relaxation function. Each relaxation function is input into the model as the sum of a Prony series,

$$f_i(x) = \sum_{k=1}^{N_i} w_{ik} \exp\left(-\frac{x}{\tau_{ik}}\right), \tag{2.10}$$

where $f_i(x)$ is the ith relaxation function, N_i is the number of Prony terms, and τ_{ik} and w_{ik} are the kth Prony time for the ith relaxation function and its weight in the sum. For a given relaxation function, the weights w_{ik} must sum to one. Since fitting an arbitrary number of Prony times and weights would be challenging, especially for inverse fitting methods, the relaxation functions are commonly represented using stretched exponential functions,

$$f_i(x) = \exp\left[-\left(\frac{x}{\tau_i}\right)^{\beta_i}\right], \tag{2.11}$$

which only requires two parameters, the characteristic time (τ_i) and breadth (β_i). After identifying τ_i and β_i, a Prony series is fit to the stretched exponential.

A material clock controls the rate of relaxation in the hereditary integrals of Eq. (2.1) by changing the relationship between the laboratory time scale ($\mathrm{d}t$) and the material time scale ($\mathrm{d}t^*$). The two time scales are related by a shift factor, a. A difference in the laboratory time $t-s$ corresponds to a difference t^*-s^* in the material time scale;

$$a\mathrm{d}t^* = \mathrm{d}t, \quad t^*-s^* = \int_s^t \frac{\mathrm{d}u}{a(u)}. \tag{2.12}$$

The shift factor is defined through a WLF-like [12] relationship, except that the relaxation rate not only depends on temperature, but also the temperature history, deformation, and deformation history;

$$\log a = \frac{-C_1 N}{C_2+N}, \tag{2.13}$$

$$\begin{aligned} N = \theta - \theta_{\mathrm{ref}} &- \int_0^t f_3\left(t^*-s^*\right)\frac{\mathrm{d}\theta}{\mathrm{d}s}\mathrm{d}s \\ &+ C_3\left(I_1 - I_{1,\mathrm{ref}} - \int_0^t f_1\left(t^*-s^*\right)\frac{\mathrm{d}I_1}{\mathrm{d}s}\mathrm{d}s\right) \\ &+ C_4\int_0^t\int_0^t f_2\left(t^*-s^*,t^*-u^*\right)\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}s}:\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u, \end{aligned} \tag{2.14}$$

where θ_{ref} is the reference temperature, C_1, C_2, C_3, and C_4 are clock parameters, and $I_{1,\mathrm{ref}}$ is the volume strain that would develop under stress-free cooling from θ_{sf} to θ_{ref},

$$I_{1,\mathrm{ref}} = \delta_\infty^{\mathrm{ref}}\left(\theta_{\mathrm{ref}} - \theta_{\mathrm{sf}}\right). \tag{2.15}$$

At the reference temperature, θ_{ref}, the equilibrium shift factor is $a=1$ such that $\mathrm{d}t = \mathrm{d}t^*$. The parameters C_1 and C_2 are related to the WLF parameters $\hat{C}_1$ and $\hat{C}_2$ [3],

$$C_1 = \hat{C}_1, \tag{2.16}$$

$$C_2 = \hat{C}_2\left(1 + C_3\delta_\infty^{\mathrm{ref}}\right). \tag{2.17}$$

Since it is easier to experimentally determine the WLF parameters, the model accepts $\hat{C}_1$ and $\hat{C}_2$ as inputs and internally converts them to the clock parameters C_1 and C_2. The clock parameter C_3 controls the magnitude of the volume strain on shift factor and the clock parameter C_4 controls the magnitude of shear strain on the shift factor. The double relaxation function in Eq. (2.14) takes the form

$$f_2(x,y) = \sum_{k=1}^{N_2} w_{ik}\exp\left(-\frac{x}{\tau_{ik}}\right)\exp\left(-\frac{y}{\tau_{ik}}\right). \tag{2.18}$$

The parameters to be identified for SPECTACULAR are listed in Table 2-1 along with their names as implemented in LAMÉ. Recall that the relaxation functions are parameterized as stretched exponentials to facilitate their identification by inverse methods, but ultimately the relaxation functions must be converted to Prony series. Even though the stretched exponential parameters τ_i and β_i are not direct model inputs, they are included in Table 2-1 since they are part of the identification procedure.

Table 2-1. List of parameters in the SPECTACULAR constitutive model.

Parameter	Name in LAMÉ
ρ	`density`
θ_{ref}	`reference temperature`
K_g^{ref}	`bulk glassy 0`
K_g'	`bulk glassy 1`
K_∞^{ref}	`bulk rubbery 0`
K_∞'	`bulk rubbery 1`
G_g^{ref}	`shear glassy 0`
G_g'	`shear glassy 1`
G_∞^{ref}	`shear rubbery 0`
G_∞'	`shear rubbery 1`
α_g^{ref}	`volcte glassy 0`
α_g'	`volcte glassy 1`
$\alpha_\infty^{\text{ref}}$	`volcte rubbery 0`
α_∞'	`volcte rubbery 1`
$\hat{C}_1$	`wlf c1`
$\hat{C}_2$	`wlf c2`
C_3	`clock c3`
C_4	`clock c4`
$\tau_1 = \tau_3$ (volume)	Not a direct input
$\beta_1 = \beta_3$ (volume)	Not a direct input
τ_2 (shear)	Not a direct input
β_2 (shear)	Not a direct input

3. EXPERIMENTAL DATA

No new experimental data was generated for this calibration effort. Instead, the model was calibrated using legacy data compiled by D.B. Adolf and stored on the Polymer Properties Database website [2]. Unfortunately, the data from Ref. [2] is highly sanitized and provides minimal information about the experimental procedures or thermomechanical history of the specimens prior to testing. Since the material behavior is highly rate- and history-dependent, reasonable assumptions regarding the experimental procedures must be made. To this end, Ref. [4] is used to infer what experimental procedures might have been used. Both the Polymer Properties Database and Ref. [4] document work by D.B. Adolf et al. on filled epoxies.

The data imported from the Polymer Properties Database was conducted on epoxy systems with the following compositions and cure schedules:

- Composition and curing of 828/CTBN/DEA/GMB:
  - 100 pbw adduct of digylcidyl ether of bisphenol A (Epon 828) and Hycar 1300x8 carboxyl terminated butadiene acrylonitrile rubber (CTBN),
  - 12 pbw diethanolamine,
  - 28 pbw 3M D32 glass microballoons (48 % by volume),
  - cured 24 h at 71 °C.
- Composition and curing of 828/DEA/GMB:
  - 100 pbw adduct of digylcidyl ether of bisphenol A (Epon 828),
  - 12 pbw diethanolamine,
  - 28 pbw 3M D32 glass microballoons (48 % by volume),
  - cured 24 h at 71 °C.

The following experiments from the Polymer Properties Database were used to calibrate both epoxy systems:

- density measured at 23 °C,
- bulk modulus at 23 °C measured by dilatometry,
- shear master curve measured with an ARES rheometer in torsion using a rectangular geometry,
- storage shear modulus measured during an isofrequency temperature sweep,
- CTE during a temperature down-up sweep measured with a TA Instruments Q400 TMA,

- heat capacity measured during a temperature down-up sweep measured with a TA Instruments Q2000 DSC (used only for the development calibration procedure in Chapter 5).

4. MODEL CALIBRATION

The calibration procedure followed these steps:

1. The shift factors from the shear master curve were used to calibrate the WLF parameters ($\hat{C}_1$, $\hat{C}_2$). The shear master curve was used to calibrate the shear relaxation function (f_2) and the shear moduli at the reference temperature (G_g^{ref}, and G_∞^{ref}). See Section 4.1.
2. The storage shear modulus measured during an isofrequency temperature sweep was used to calibrate the temperature derivatives of the shear moduli (G_g', G_∞'). The reference values of the shear moduli (G_g^{ref}, G_∞^{ref}) can also be updated at this step. See Section 4.2.
3. The bulk moduli parameters (K_g^{ref}, K_g', K_∞^{ref}, K_∞') were estimated from a composite theory analysis. The results were adjusted to make sure the room temperature glassy shear modulus matched the value measured from dilatometry. See Section 4.3.
4. The CTEs (α_g^{ref}, α_g', $\alpha_\infty^{\text{ref}}$, α_∞') and the thermal strain relaxation function (f_3) were calibrated using the CTE measured by a TMA during a stress-free temperature sweep. It was assumed that the volumetric and thermal strain relaxation functions were the same ($f_1 = f_3$). Inverse parameter identification was deployed where finite element simulations in Sierra/SM were used to iteratively evaluate the forward problem. See Section 4.4.
5. The shear strain clock parameter (C_4) was fit to stress–strain curves in glassy compression at three different temperatures. Glassy shear modulus parameters (G_g^{ref}, G_g') can also be updated to match the glassy Young's modulus. Inverse parameter identification was deployed where finite element simulations in Sierra/SM were used to iteratively evaluate the forward problem. See Section 4.5.

Two parameters were fixed from the outset, so are not included in the calibration procedure. The Polymer Properties Database gives the room temperature densities as $\rho = 770\,\text{kg/m}^3$ for 828/CTBN/DEA/GMB and $\rho = 760\,\text{kg/m}^3$ for 828/DEA/GMB. The constitutive model does not use ρ in any calculations, but the parameter is needed for the development calibration (see Chapter 5) to convert heat capacities from per volume units (as calculated in Sierra) to per mass units (as measured in experiments). No data was available to calibrate C_3, so a reasonable estimate was chosen $C_3 = 1000\,\text{K}$ [3, 5].

When needed, parameter optimization was conducted using Dakota Version 6.15 [13]. When the optimization algorithm used a random seed (such as a genetic algorithm), the algorithm was repeated three times and the best outcome from all three attempts was chosen. This was done to reduce the possibility that a bad seed produced a sub-optimal fit. When finite element analysis was used for parameter fitting, Sierra/SM 5.4 [11] was used with the `spectacular` model in LAMÉ 5.4 [6]. All finite element analyses used single element calculations (i.e. the deformation and temperature fields are assumed to be homogeneous).

4.1. Shear master curve

The calibration process begins with an analysis of the shear master curve. To construct the master curve, the storage and loss moduli are measured in torsion during frequency sweeps at various constant temperatures. Time–temperature superposition is used to shift the moduli measured at different temperatures to a single reference temperature in order to form a single master curve. There is some flexibility in the choice of reference temperature, but it should be chosen so that equilibrated behavior can be assured at that temperature. Since data from all other temperatures are shifted to the reference temperature to construct the master curve, the shift factor at the reference temperature is, by definition, one. The WLF parameters, $\hat{C}_1$ and $\hat{C}_2$, are fit to the shift factors used to construct the shear master curve. Then, the shear master curve is used to calibrate the shear relaxation function, f_2, and the glassy and rubbery limits of the shear moduli at the reference temperature, G_g^{ref} and G_∞^{ref}. The shear master curve is constructed in the frequency domain, so fitting f_2 typically involves converting from the time domain to the frequency domain. However, the shear master curve data from the Polymer Properties Database has already been converted into the time domain, greatly simplifying the fitting procedure for f_2. It should be noted that the values of G_g^{ref} and G_∞^{ref} extracted from the shear master curve did not produce good agreement with the Young's modulus measured in glassy compression. Therefore G_g^{ref} and G_∞^{ref} were calibrated from other experiments that produced better predictions of the glassy Young's modulus. The exception was G_∞^{ref} for 828/CTBN/DEA/GMB, which was kept from the master curve, since a better source was not available.

The shear master curve for 828/CTBN/DEA/GMB was constructed at a reference temperature of $\theta_{\text{ref}} = 65\,^\circ\text{C}$ and the shear master curve for 828/DEA/GMB was constructed at a reference temperature of $\theta_{\text{ref}} = 75\,^\circ\text{C}$. The WLF parameters were calibrated by fitting the WLF function [12],

$$\log a = \frac{-\hat{C}_1\,(\theta - \theta_{\text{ref}})}{\hat{C}_2 + (\theta - \theta_{\text{ref}})}, \tag{4.1}$$

to the shift factors used to construct the shear master curve. Shift factors for which $\log a \geq 1$ were ignored, as the material is unlikely to be in equilibrium at these shift factors and thus WLF behavior is not expected. The fitting was carried out in Dakota using the `conmin_frcg` method, which is a conjugate gradient optimization algorithm. The objective function was formed using the L_2 norm of the absolute error between the experimentally measured $\log a$ and the $\log a$ calculated by the WLF equation, Eq. (4.1). The bounds, initial point, and results for the optimization method are given in Table 4-1 for 828/CTBN/DEA/GMB and Table 4-2 for 828/DEA/GMB. Plots of the WLF fit versus experimental shift factors are shown in Fig. 4-1.

The shear relaxation function and the glassy and rubbery limits of the shear modulus at the reference temperature were fit to the master curve. The experimental data was already available in the time domain, so the function

$$G(t) = \left(G_g^{\text{ref}} - G_\infty^{\text{ref}}\right) \exp\left[-\left(\frac{t}{\tau_2}\right)^{\beta_2}\right] + G_\infty^{\text{ref}} \tag{4.2}$$

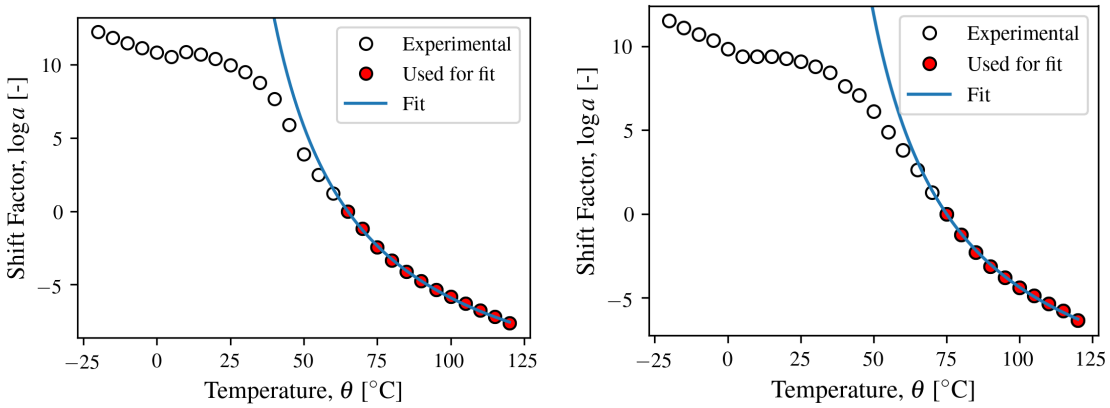
was directly fit to the data. Fitting was carried out in Dakota using the `soga` method (single objective genetic algorithm). The genetic algorithm was executed using a population size of 100

Table 4-1. WLF parameters fit to the measured shift factors versus temperature for 828/CTBN/DEA/GMB. The parameters were fit using the `conmin_frcg` in Dakota. The bounds and initial point used by the method are also listed.

Parameter	Lower bound	Upper bound	Initial point	Result	Units
$\hat{C}_1$	1	50	25.5	14.9	–
$\hat{C}_2$	1	100	50.5	53.4	K

Table 4-2. WLF parameters fit to the measured shift factors versus temperature for 828/DEA/GMB. The parameters were fit using the `conmin_frcg` in Dakota. The bounds and initial point used by the method are also listed.

Parameter	Lower bound	Upper bound	Initial point	Result	Units
$\hat{C}_1$	1	50	25.5	13.8	–
$\hat{C}_2$	1	100	50.5	53.9	K



(a) 828/CTBN/DEA/GMB **(b) 828/DEA/GMB**

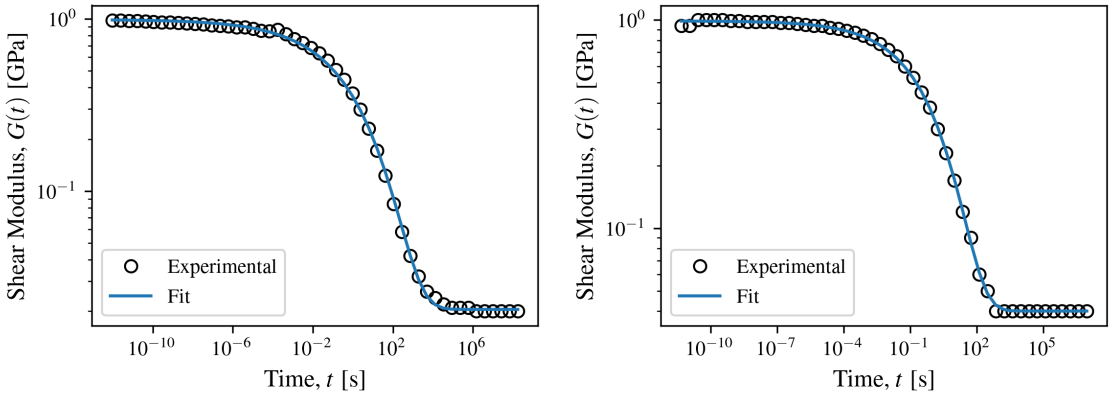
Figure 4-1. WLF function fit to shift factors used to construct the shear master curve.

Table 4-3. Parameters fit to the shear master curve of 828/CTBN/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times. The symbol † indicates a value that was not used in the final parameter set due to conflicts with other experimental data.

Parameter	Lower bound	Upper bound	Run 1	Run 2 BEST	Run 3	Units
$\log(\tau_2/\mathrm{s})$	-3	3	0.0941	-0.158	0.003 28	–
β_2	0.1	0.5	0.215	0.192	0.207	–
G_g^{ref}	0.5	1.0	0.945	$0.993^{\dagger}$	0.970	GPa
G_∞^{ref}	1	50	20.594	20.495	20.752	MPa
Objective			0.299	0.239	0.247	–

Table 4-4. Parameters fit to the shear master curve of 828/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times. The symbol † indicates a value that was not used in the final parameter set due to conflicts with other experimental data.

Parameter	Lower bound	Upper bound	Run 1	Run 2 BEST	Run 3	Units
$\log(\tau_2/\mathrm{s})$	-3	3	-0.122	-0.180	-0.0933	–
β_2	0.1	0.5	0.261	0.253	0.260	–
G_g^{ref}	0.5	1.0	0.981	$0.989^{\dagger}$	0.972	GPa
G_∞^{ref}	1	50	39.804	$40.088^{\dagger}$	39.918	MPa
Objective			0.146	0.134	0.173	–



(a) 828/CTBN/DEA/GMB **(b) 828/DEA/GMB**

Figure 4-2. Shear master curve fit

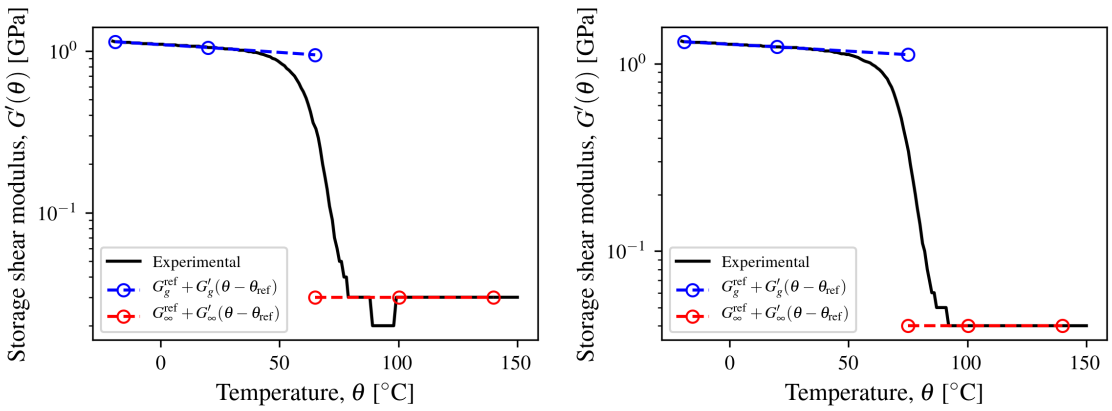
over 100 generations. Since genetic algorithms utilize randomness, the algorithm was run three times to reduce the risk of a bad seed producing a sub-optimal fit. The objective function for the optimization was formed using the L_2 norm of the relative error between Eq. (4.2) and the experimental data. It was important to use the relative error given that the shear modulus changes by nearly two orders of magnitude; using an absolute error causes the rubbery shear modulus to have a negligible impact on the objective function. The bounds used for the optimization along with the results from each of the three executions are listed in Table 4-3 for 828/CTBN/DEA/GMB and Table 4-4 for 828/DEA/GMB. Since characteristic times in stretched exponential can vary by orders of magnitude, $\log(\tau_2/\mathrm{s})$ was optimized instead of τ_2 itself. The parameter sets with the lowest objective functions were progressed to the next calibration stage. The fits to the shear master curve are shown in Fig. 4-2.

4.2. Storage shear modulus measured during an isofrequency temperature sweep

The parameters for the shear modulus can be calibrated from the shear storage modulus measured under oscillatory torsion during an isofrequency temperature sweep. The experimental results are shown in Fig. 4-3. The cold and hot limits of the shear storage modulus approximately represent $G_g(\theta)$ and $G_\infty(\theta)$ Therefore, the linear temperature dependence of $G_g(\theta)$ and $G_\infty(\theta)$ correspond to the slopes at the ends of the curve in Fig. 4-3 and the reference values are found by extrapolating the linear cold and hot limits to the reference temperature. A graphical representation of this analysis is shown in Fig. 4-3, where, for both the cold and hot limits, two points are chosen to calculate the slope of the line, and a third point is extrapolated to the reference temperature. The results from this analysis are presented in Table 4-5. Comparing Tables 4-3, 4-4 and 4-5 reveals that the reference values for the shear moduli do not necessarily agree between the two experiments. For 828/CTBN/DEA/GMB, neither set of shear modulus parameters produced good agreement with the Young's modulus in glassy compression. Therefore G_∞^{ref} is taken from the master curve (Table 4-3) and G'_∞ is taken from the isofrequency temperature sweep (Table 4-5) and the glassy shear moduli parameters G_g^{ref} and G'_g are fit directly to glassy compression data. For 828/DEA/GMB, the shear parameters determined from the isofrequency temperature sweep do produce a good fit to the Young's modulus in glassy compression, so these parameters are incorporated into the final parameter set.

Table 4-5. Shear modulus parameters determined from the shear storage modulus measured under oscillatory torsion during an isofrequency temperature sweep. The symbol † indicates a value that was not used in the final parameter set due to conflicts with other experimental data.

Parameter	828/CTBN/DEA/GMB	828/DEA/GMB	Units
G_g^{ref}	$0.947^{\dagger}$	1.118	GPa
G_g'	$-2^{\dagger}$	-2	MPa/K
G_∞^{ref}	$30^{\dagger}$	40	MPa
G_∞'	0	0	MPa/K



(a) 828/CTBN/DEA/GMB **(b) 828/DEA/GMB**

Figure 4-3. Shear storage modulus during an isofrequency temperature sweep. Two points are chosen from the glassy limit and extrapolated to the reference temperature to estimate G_g^{ref} and G_g' (blue circles). Two points are chosen from the rubbery limit and extrapolated to the reference temperature to estimate G_∞^{ref} and G_∞' (red circles).

4.3. Bulk modulus from dilatometry and composite theory

The Polymer Properties Database provides the bulk modulus at room temperature (23 °C) as measured by dilatometry and ultrasound. Since the two measurements are reasonably close, the dilatometry value is arbitrarily chosen for parameter identification purposes. However, the bulk modulus at a single temperature is not sufficient to parameterize the glassy and rubbery bulk moduli, each with the possibility for a linear temperature dependence. Therefore, a simple composite theory [14] was deployed to calculate the bulk moduli for the filled epoxies using the properties of the unfilled epoxies,

$$K(\theta) = K_p(\theta) + \frac{\big(K_f - K_p(\theta)\big)\,\phi_f}{\left[1 + \frac{\big(1-\phi_f\big)\big(K_f - K_p(\theta)\big)}{K_p(\theta) + \frac{4}{3}G_p(\theta)}\right]}, \tag{4.3}$$

where $K(\theta)$ is the bulk modulus of the filled epoxy, $K_p(\theta)$ and $G_p(\theta)$ are the bulk and shear moduli of the unfilled ("pure") epoxy, K_f is the bulk modulus of the filler particles, and ϕ_f is the filler volume fraction. For both filled epoxy systems $\phi_f = 0.48$ and K_f is chosen to ensure that $K_g(23\,^\circ\text{C})$ matches value measured by dilatometry (to within $\pm 0.1\,\text{GPa}$).

The properties of 828/DEA were taken from Table 3 of Ref. [3],

$$\text{(For 828/DEA)} \quad K_{p,g}(\theta) = 4.9\,\text{GPa} - (12\,\text{MPa/K})\,(\theta - 75\,^\circ\text{C}) \tag{4.4}$$

$$G_{p,g}(\theta) = 0.9\,\text{GPa} - (4.2\,\text{MPa/K})\,(\theta - 75\,^\circ\text{C}) \tag{4.5}$$

$$K_{p,\infty}(\theta) = 3.2\,\text{GPa} - (12\,\text{MPa/K})\,(\theta - 75\,^\circ\text{C}) \tag{4.6}$$

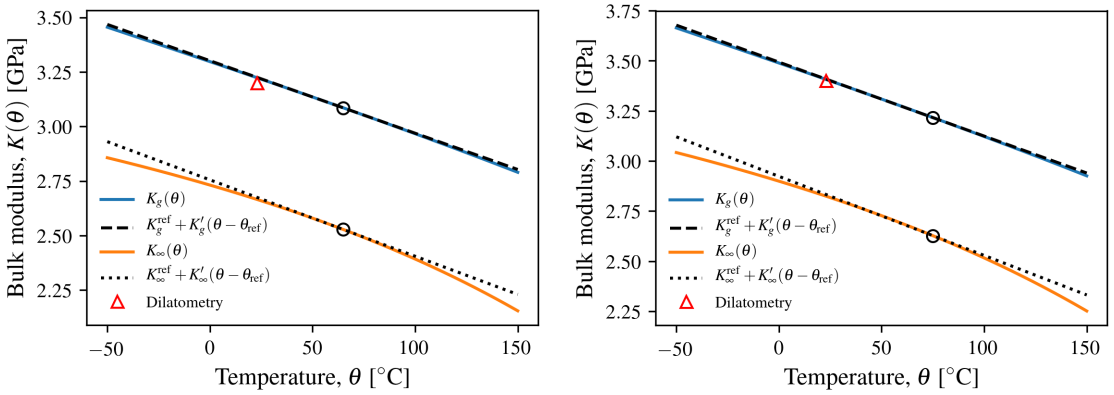
$$G_{p,\infty}(\theta) = 4.5\,\text{MPa}. \tag{4.7}$$

When Eqs. (4.4) and (4.5) along with $K_f = 2.2\,\text{GPa}$ are plugged into Eq. (4.3), the resulting $K_g(\theta)$ for 828/DEA/GMB matches the bulk modulus measured by dilatometry at room temperature, $K_g(23\,^\circ\text{C}) = 3.4\,\text{GPa}$. Then, $K_\infty(\theta)$ for 828/DEA/GMB is computed using Eqs. (4.6) and (4.7) in Eq. (4.3). The functions $K_g(\theta)$ and $K_\infty(\theta)$ are then linearized about θ_{ref} so they can be parameterized using the form required by the model, see Eq. (2.3).

The same analysis was conducted for 828/CTBN/DEA/GMB, but many assumptions about the unfilled behavior were necessary given that no information was available for 828/CTBN/DEA on the Polymer Properties Database. First, it was assumed that the temperature dependence of the glassy and rubbery bulk moduli were the same for 828/DEA and 828/CTBN/DEA. Second, it was assumed that the room temperature bulk modulus of 828/CTBN/DEA was the same as that of 826/CTBN/DEA, which was determined by dilatometry to be 4.61 GPa. These assumptions about the room temperature bulk modulus and its temperature dependence were used to approximate the glassy bulk modulus at the reference temperature, 65 °C. Third, the reference value for the rubbery bulk modulus was then estimated by assuming that the ratio $K_\infty^{\text{ref}}/K_g^{\text{ref}}$ is the same for both 828/DEA and 828/DEA/CTBN. Finally, shear master curves and the shear modulus under an isofrequency temperature sweep from the Polymer Properties Database for 826/CTBN/DEA were used to approximate the unfilled glassy and rubbery shear moduli of 828/CTBN/DEA as functions of temperature following the procedures outlined in Sections 4.1 and 4.2. From these

Table 4-6. Bulk modulus parameters determined from the composite analysis.

Parameter	828/CTBN/DEA/GMB	828/DEA/GMB	Units
K_g^{ref}	3.1	3.2	GPa
K_g'	-3.3	-3.7	MPa/K
K_∞^{ref}	2.5	2.6	GPa
K_∞'	-3.5	-3.9	MPa/K



(a) 828/CTBN/DEA/GMB **(b) 828/DEA/GMB**

Figure 4-4. Results from the bulk modulus composite analysis compared to the bulk modulus measured at room temperature. The functions are linearized about the reference temperature (black circles) to determine model parameters.

assumptions, the equations for the bulk and shear moduli for unfilled 828/CTBN/DEA are taken as

$$\text{(For 828/CTBN/DEA)} \quad K_{p,g}(\theta) = 5.1\,\text{GPa} - (12\,\text{MPa/K})\,(\theta - 65\,^\circ\text{C}) \tag{4.8}$$

$$G_{p,g}(\theta) = 0.779\,\text{GPa} - (3.4\,\text{MPa/K})\,(\theta - 65\,^\circ\text{C}) \tag{4.9}$$

$$K_{p,\infty}(\theta) = 3.3\,\text{GPa} - (12\,\text{MPa/K})\,(\theta - 65\,^\circ\text{C}) \tag{4.10}$$

$$G_{p,\infty}(\theta) = 4\,\text{MPa}. \tag{4.11}$$

When Eqs. (4.8) and (4.9) along with $K_f = 2.0\,\text{GPa}$ are plugged into Eq. (4.3), the resulting $K_g(\theta)$ for 828/CTBN/DEA/GMB matches the bulk modulus measured by dilatometry, $K_g(23\,^\circ\text{C}) = 3.2\,\text{GPa}$. Then, $K_\infty(\theta)$ for 828/CTBN/DEA/GMB is computed using Eqs. (4.10) and (4.11) in Eq. (4.3). Just as before, $K_g(\theta)$ and $K_\infty(\theta)$ are then linearized about θ_{ref} for parameterization following the form required by the model, see Eq. (2.3). Using both 826/CTBN/DEA and 828/DEA to approximate various parameters for 828/CTBN/DEA invites additional scrutiny regarding the bulk modulus parameters determined by this analysis for 828/CTBN/DEA/GMB. Obviously, it would be desirable to obtain more accurate information on the bulk modulus for 828/CTBN/DEA/GMB, either through measurements for the bulk modulus of 828/CTBN/DEA then re-calculating values using the composite analysis, or through direct bulk modulus measurements on 828/CTBN/DEA/GMB. However, in the absence of better information, the approximation is defended on the basis that the bulk modulus measured at room temperature for 828/CTBN/DEA/GMB is matched by the composite analysis, and it is matched using a GMB filler bulk modulus within 10 % of the value determined for 828/DEA/GMB, where much better information about the unfilled bulk modulus was available.

The functions $K_g(\theta)$ and $K_\infty(\theta)$ computed from the composite theory for both epoxy systems along with their linearized forms are shown in Fig. 4-4. The resulting bulk modulus parameters are shown in Table 4-6. Note that $K_f = 2.0\,\text{GPa}$ was required for 828/CTBN/DEA/GMB to match the experimentally measured room temperature bulk modulus and $K_f = 2.2\,\text{GPa}$ was required for 828/DEA/GMB to match the experimentally measured room temperature bulk modulus. However, both systems are filled with the same 3M D32 glass microballoons. To further complicate the matter, Ref. [4] calculates $K_f = 2.8\,\text{GPa}$ for 3M D32 glass microballoons. The source of these discrepancies was not investigated, but has been noted here for clarity.

4.4. Coefficient of thermal expansion during a stress-free temperature sweep

The transition from the rubbery coefficient of thermal expansion (CTE) to the glassy CTE measured by a TMA during a stress-free temperature sweep can be used to calibrate the thermal-volumetric (thermal strain) relaxation function (f_3) and the CTE parameters (α_g^{ref}, α_g', $\alpha_\infty^{\text{ref}}$, α_∞'). Inverse methods deploying finite element simulations are needed to identify the parameters that best fit the experimental data.

The temperature sweep in a TMA was simulated in Sierra/SM using a single element. The thermal history in the finite element simulation was designed to match the experiment as closely as possible. However, some information about the experimental procedures were missing on the

Table 4-7. Parameters fit to the CTE during a stress-free temperature sweep for 828/CTBN/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times.

Parameter	Lower bound	Upper bound	Run 1 BEST	Run 2	Run 3	Units
$\log(\tau_3/\mathrm{s})$	-2	4	3.21	3.33	3.22	–
β_3	0.15	0.5	0.268	0.263	0.268	–
α_g^{ref}	50	220	113	113	115	$10^{-6}/\mathrm{K}$
α_g'	0	2	0	0	0	$10^{-6}/\mathrm{K}^2$
$\alpha_\infty^{\mathrm{ref}}$	280	380	333	333	331	$10^{-6}/\mathrm{K}$
α_∞'	0	1	0.8	0.8	0.9	$10^{-6}/\mathrm{K}^2$
Objective			227.5	229.1	228.3	$10^{-6}/\mathrm{K}$

Table 4-8. Parameters fit to the CTE during a stress-free temperature sweep for 828/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times.

Parameter	Lower bound	Upper bound	Run 1	Run 2 BEST	Run 3	Units
$\log(\tau_3/\mathrm{s})$	-2	4	0.447	0.428	0.444	–
β_3	0.15	0.5	0.257	0.256	0.255	–
α_g^{ref}	50	220	84.2	83.8	83.5	$10^{-6}/\mathrm{K}$
α_g'	0	1	0	0	0	$10^{-6}/\mathrm{K}^2$
$\alpha_\infty^{\mathrm{ref}}$	280	380	295	296	296	$10^{-6}/\mathrm{K}$
Objective			254.000	253.618	253.649	$10^{-6}/\mathrm{K}$

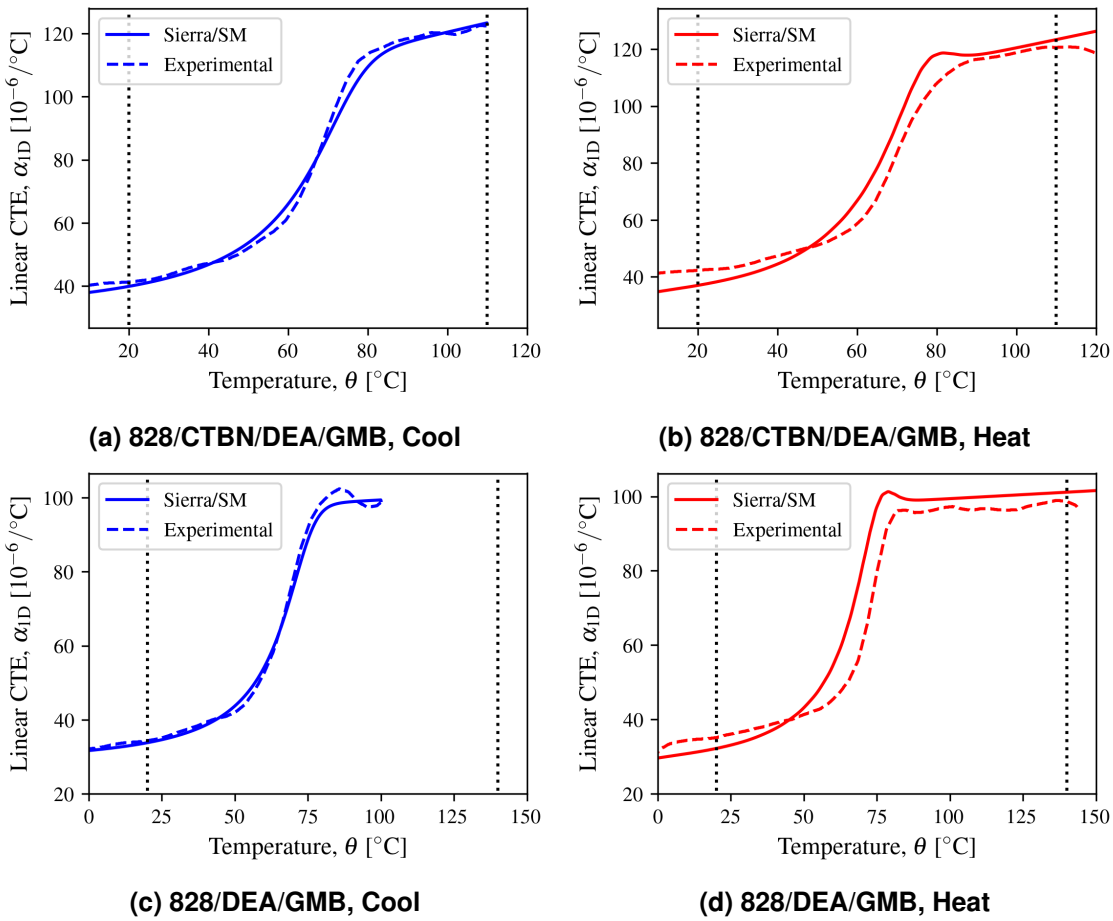


Figure 4-5. Coefficient of thermal expansion (CTE) during a stress-free temperature sweep simulated by Sierra/SM. Parameters were optimized to fit the experimental data obtained from a thermomechanical analyzer (TMA).

Polymer Properties Database website. Unknown details of the experiments were assumed to match those reported in Ref. [4], which also describes work conducted by D.B. Adolf on filled epoxies. For 828/CTBN/DEA/GMB, the simulation starts at 100 °C, cools to −9 °C, and then reheats to 150 °C. For 828/DEA/GMB, the simulation starts at 110 °C, cools to 0 °C, and then reheats to 130 °C. The heating and cooling rates are unknown, but are assumed to be 2 °C/min. Between the cooling and heating steps, the temperature was held for 5 min.

Six parameters were fit: all four CTE parameters (α_g^{ref}, α_g', $\alpha_\infty^{\text{ref}}$, α_∞') and two parameters for thermal-volumetric relaxation function parameterized as a stretched exponential (τ_3 and β_3). The characteristic time τ_3 was optimized in log space, since τ_3 may vary by orders of magnitude. The rubbery CTE parameters can be extracted directly from the data, so inverse identification is not strictly necessary, but was carried out anyways for consistency with the other parameters identified from this step. On the other hand, the best glassy CTE parameters may vary somewhat from the apparent values from the experimental curves, since the apparent glassy behavior is dependent on the thermomechanical history. Therefore, inverse identification is advantageous for

the parameters related to the glassy CTE limit. It is assumed that the volumetric and thermal-volumetric relaxation functions are the same, $f_1 = f_3$. This assumption is embedded into SPEC, but is not necessary in SPECTACULAR. However, it is challenging to obtain independent data for f_1.

The parameter identification is conducted in Dakota using the `soga` method with a population size of 100 over 100 generations. The objective function considered the L_2 norm of the absolute error between the simulated and experimental CTEs on both heating and cooling. The data during cooling is given twice the weight in the objective function as this is the more important behavior for modeling residual stress development. Data from heating is still considered because unrealistically high CTEs are predicted during the glassy-to-rubbery transition during reheating if heating is completely ignored in the objective function. For 828/CTBN/DEA/GMB, the objective function only considers data between 20 °C and 110 °C. For 828/DEA/GMB, the objective function is calculated using data from 20 °C to 140 °C. To reduce the possibility that a bad random seed creates a sub-optimal fit, the analysis is conducted three times. The resulting parameters from the fits are shown in Tables 4-7 and 4-8. Plots of the simulated CTEs compared to experimental measurements are shown in Fig. 4-5.

4.5. Glassy compression

In SPECTACULAR yield emerges from shear contributions to the shift factor that act to accelerate relaxations. The magnitude of this effect is controlled by C_4, so this parameter is typically calibrated from uniaxial compression below T_g, i.e. glassy compression. For 828/DEA/GMB, only C_4 was calibrated at this stage, since the shear modulus obtained from the isofrequency temperature sweep produced a good match to the Young's modulus under glassy compression (see the results from this step in Fig. 4-6b). However, for 828/CTBN/DEA/GMB, the glassy Young's modulus was not well matched from previously calibrated shear modulus parameters, so G_g^{ref} and G_g' were also calibrated using glassy compression experiments.

This fitting step is carried out using inverse parameter identification deploying finite element simulations in Sierra/SM to evaluate the objective function. It is important to simulate the thermal history of the specimen prior to compression, but the details of the experiments were not listed on the Polymer Properties Database website. Once again, the experimental procedures from Ref. [4] were used to fill in the missing information. The simulations start at the reference temperature and are cooled at 1 °C/min to the loading temperature (either 23 °C, 45 °C, or 55 °C). The temperature is held at the loading temperature for 10 min and then the material is compressed at a nominal strain rate of 1 %/s.

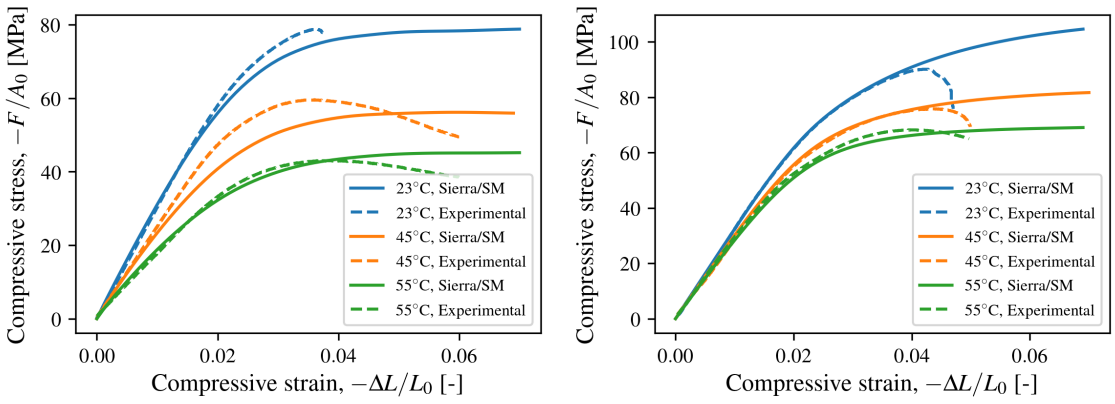
For 828/CTBN/DEA/GMB, the identification was conducted using the `soga` method from Dakota with a population size of 100 over 100 generations. It was tricky to determine an objective function that was not dominated by either matching the Young's modulus or the yield stress. Calculating the objective function as the sum of the L_2 norms of the relative errors between the Young's modulus, yield stress (maximum nominal stress), and stress–strain curves up to yield for all three loading temperatures produced the most satisfactory fit. Again, to mitigate the impact of bad random seeds, the genetic algorithm was repeated three times. The parameters fit from glassy

Table 4-9. Parameters fit to glassy compression at three different temperatures for 828/CTBN/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times.

Parameter	Lower bound	Upper bound	Run 1 BEST	Run 2	Run 3	Units
C_4	0	100 000	14 600	14 800	14 900	K
G_g^{ref}	0.9	1.2	1.089	1.096	1.092	GPa
G_g'	−20	0	−9.2	−9.4	−9.6	MPa/K
Objective			0.4688	0.4689	0.4699	–

Table 4-10. Parameters fit to glassy compression at three different temperatures for 828/DEA/GMB. The parameters were fit using the `conmin_frcg` method in Dakota. The bounds and initial point used by the method are also listed.

Parameter	Lower bound	Upper bound	Initial point	Result	Units
C_4	0	100 000	50 000	19 600	K



(a) 828/CTBN/DEA/GMB **(b) 828/DEA/GMB**

Figure 4-6. Stress–strain response under glassy uniaxial compression simulated by Sierra/SM. Parameters were optimized to fit the experimental data at loading temperatures of 23 °C, 45 °C, **and** 55 °C.

compression for 828/CTBN/DEA/GMB are listed in Table 4-9. For 828/DEA/GMB, the identification of a single parameter was much simpler. The `conmin_frcg` method in Dakota was used and the objective function was calculated from the L_2 norm of the relative error of the stress–strain curves from all three temperatures. The resulting value for C_4 is listed in Table 4-10. Plots of the best fit stress–strain curves are shown in Fig. 4-6.

4.6. Calibrated parameters and discussion

The calibrated parameters for 828/CTBN/DEA/GMB and 828/DEA/GMB are listed in Table 4-11 along with parameters from a previous calibration for 828/DEA/GMB from SAND2011-4751 [1]. Graphical calibration summaries are shown in Figs. 4-7, 4-8, and 4-9 for 828/CTBN/DEA/GMB, 828/DEA/GMB, and the legacy 828/DEA/GMB calibration. These graphical summaries compare fits and predictions from each calibration to all experimental data used from the Polymer Properties Database. Plots of relaxation functions are also included in the graphical calibration summaries, where the Prony series input into the model (lines) are compared to the stretched exponentials (circles) used to conveniently parameterize the relaxation functions. The complete material definitions for use with Sierra/SM are given in Appendices A, B, and C for 828/CTBN/DEA/GMB, 828/DEA/GMB, and the legacy 828/DEA/GMB calibration, respectively.

The step-by-step calibration procedure used to produce the two new calibrations minimizes coupling between steps so that later calibration steps have minimal impact on fits obtained from previous steps. Therefore, most of the plots in Figs. 4-7 and 4-8 are identical to the plots presented as the calibrations were developed. However, the glassy shear modulus parameters G_g^{ref} and G_g' were chosen to best fit the Young's modulus under sub-T_g compression, so updated fits to the shear master curve and isofrequency temperature sweep should be addressed. For 828/CTBN/DEA/GMB, the glassy shear modulus was optimized to match Young's modulus in glassy compression, see Fig. 4-7g. This results in a higher G_g^{ref} than was measured from the shear master curve (see Fig. 4-7b) and both G_g^{ref} and G_g' are higher than the values determined from the isofrequency temperature sweep (see Fig. 4-7c). For 828/DEA/GMB, the values of G_g^{ref} and G_g' determined from the isofrequency temperature sweep (see Fig. 4-8c) gave satisfactory predictions for the glassy Young's modulus (see Fig. 4-8g). However, the final value of G_g^{ref} was higher than measured by the master curve (see Fig. 4-8b). The spread in values for G_g^{ref} are limited to 15 %, but the value of G_g' for 828/CTBN/DEA/GMB varies by approximately a factor of 4 between the isofrequency temperature sweep and the value optimized to fit the Young's modulus.

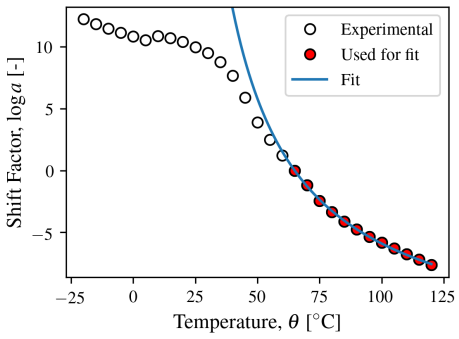
The current and legacy calibrations for 828/DEA/GMB are reasonably alike. This is not surprising since a visual inspection of the data in SAND2011-4751 [1] indicates that both calibrations were fit to the same legacy experiments now saved in the Polymer Properties Database. However, there are a few significant differences between the two parameter sets. First, the legacy calibration treats the bulk modulus as a temperature and time independent constant, while the current calibration estimates rubbery and glassy limits and temperature dependence from limited information, see Figs. 4-8d and 4-9d. Second, the volumetric relaxation function $f_1 = f_3$ for the legacy calibration is much broader and has a longer characteristic time than the

Table 4-11. Calibrated parameters for 828/CTBN/DEA/GMB and 828/DEA/GMB. A legacy calibration or 828/DEA/GMB from SAND2011-4751 [1] is included for comparison.

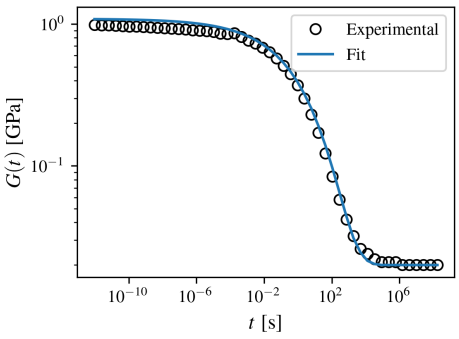
Parameter	828/CTBN/ DEA/GMB	828/DEA/GMB	828/DEA/GMB Ref. [1]	Units
ρ	770	760	750	$\mathrm{kg/m^3}$
θ_{ref}	65	75	75	°C
K_g^{ref}	3.1	3.2	3.35	GPa
K_g'	−3.3	−3.7	0	MPa/K
K_∞^{ref}	2.5	2.6	3.35	GPa
K_∞'	−3.5	−3.9	0	MPa/K
G_g^{ref}	1.089	1.118	1.2	GPa
G_g'	−9.2	−2	−1	MPa/K
G_∞^{ref}	20	40	40	MPa
G_∞'	0	0	0	MPa/K
α_g^{ref}	113	84	81	10^{-6}/K
α_g'	0	0	0.1	$10^{-6}/\mathrm{K}^2$
$\alpha_\infty^{\mathrm{ref}}$	333	296	285	10^{-6}/K
α_∞'	0.8	0.1	0.07	$10^{-6}/\mathrm{K}^2$
$\hat{C}_1$	14.9	13.8	12.5	–
$\hat{C}_2$	53.4	53.9	45.4	K
C_3	1000	1000	1000†	K
C_4	14600	19600	17500	K
$\tau_1 = \tau_3$ (volume)	1606	2.68	20	s
$\beta_1 = \beta_3$ (volume)	0.268	0.256	0.15	–
τ_2 (shear)	0.695	0.661	0.5	s
β_2 (shear)	0.192	0.253	0.231	–

current calibration. This is evident from the CTE predicted by the legacy calibration in Figs. 4-9e and 4-9f, where the transition is overly broad. It is worth mentioning that the CTE fit portrayed in SAND2011-4751 is also too broad (see Fig. 2-11 of SAND2011-4751 [1]). Comparatively, the new parameters for 828/DEA/GMB fit the CTE data much better, see Figs. 4-8e and 4-8f.

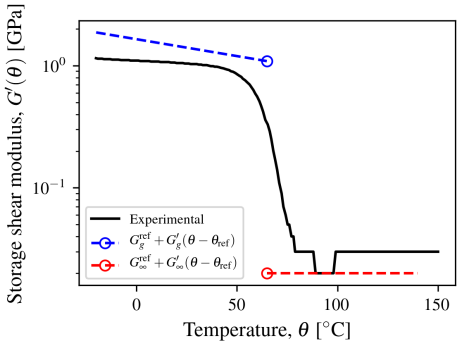
Inverse methods using finite element simulations were deployed to fit the CTE measured by a TMA as well as the stress–strain curves under uniaxial compression. Since the necessary experimental details for running these simulations was not found on the Polymer Properties Database, experimental procedures from Ref. [4] were used instead. These simulations were also used to create the predictions for the legacy calibrations in Figs. 4-9e, 4-9f, and 4-9g. When the recent predictions from the legacy calibrations are compared to predictions from the report documenting that calibration, the results seem similar, compare Figs. 4-9f, and 4-9g in the current report to Figs. 2-11 and 2.12 in SAND2011-4751 [1]. This would indicate that the assumptions used to build to simulations are reasonably accurate.



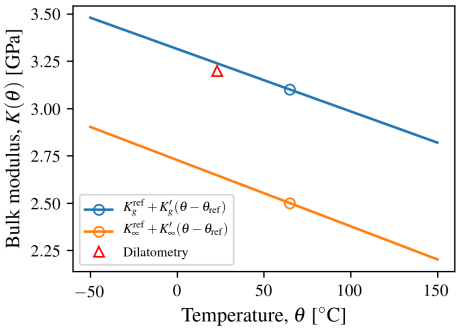
(a) WLF from shear master curve.



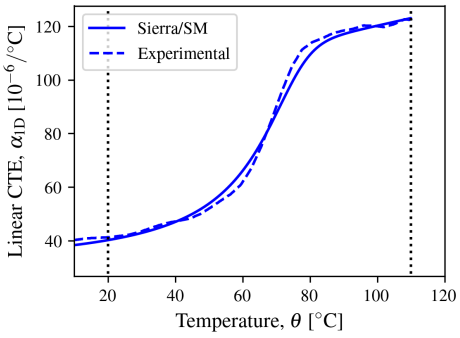
(b) Shear master curve



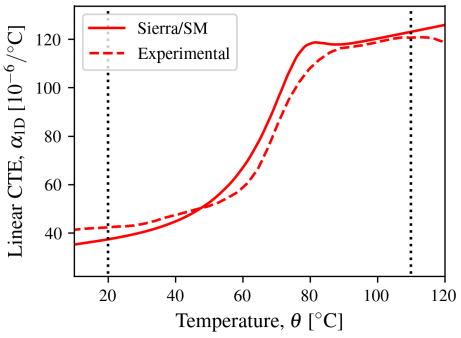
(c) Shear modulus vs. temperature



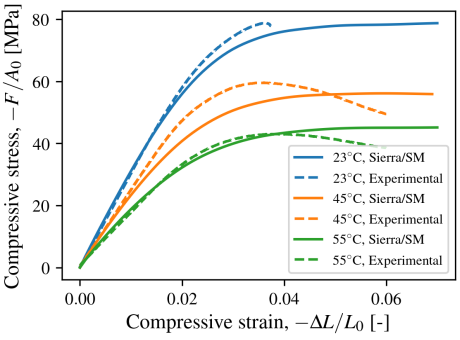
(d) Bulk modulus vs. temperature



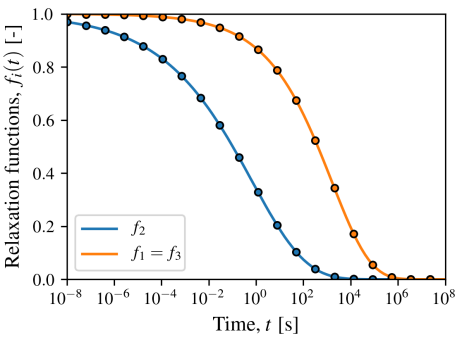
(e) CTE during cooling



(f) CTE during heating

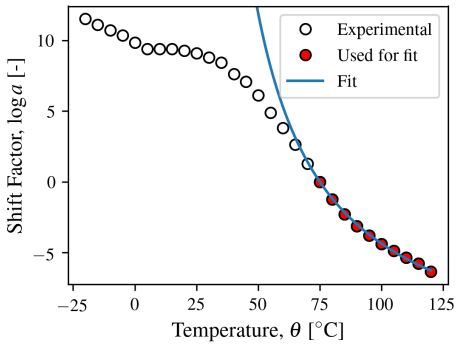


(g) Uniaxial compression

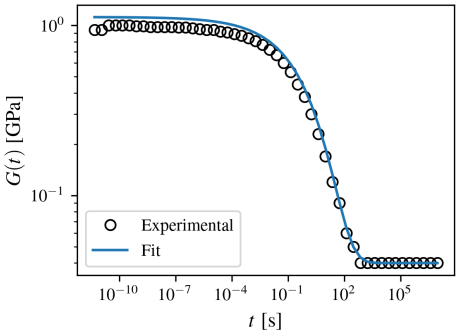


(h) Relaxation functions

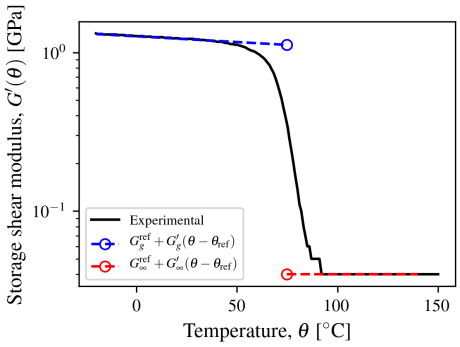
Figure 4-7. 828/CTBN/DEA/GMB graphical calibration summary.



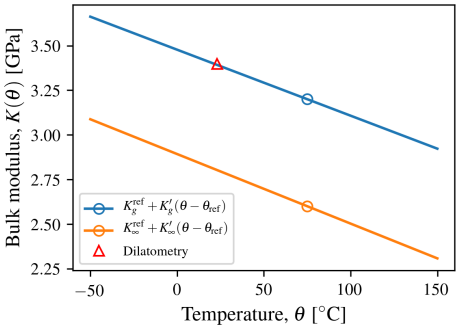
(a) WLF from shear master curve.



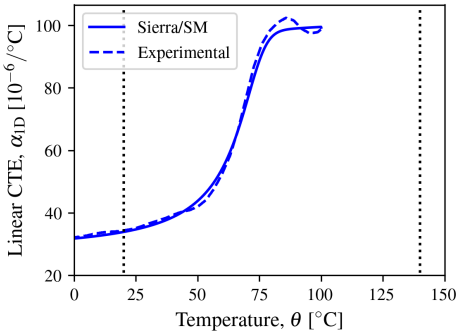
(b) Shear master curve



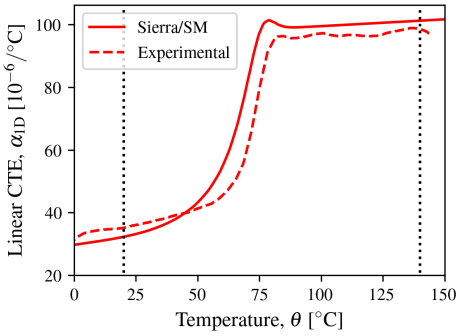
(c) Shear modulus vs. temperature



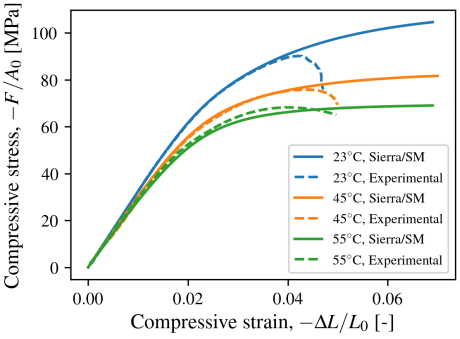
(d) Bulk modulus vs. temperature



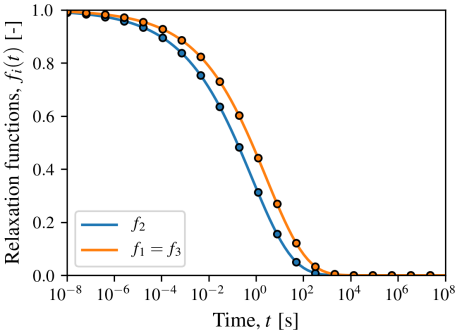
(e) CTE during cooling



(f) CTE during heating

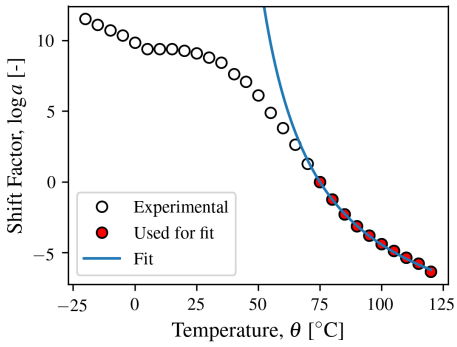


(g) Uniaxial compression

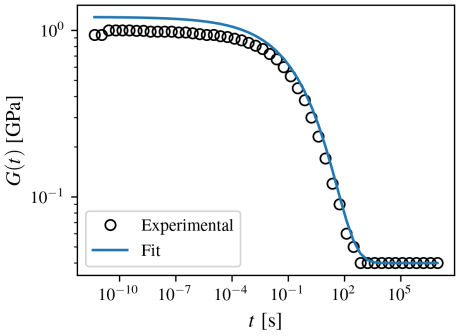


(h) Relaxation functions

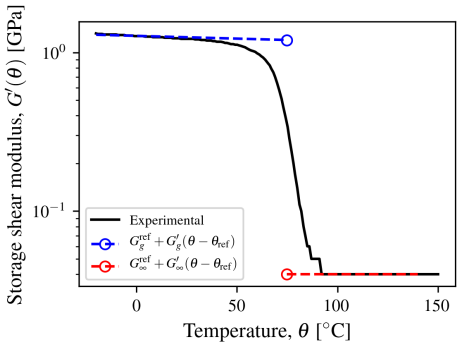
Figure 4-8. 828/DEA/GMB graphical calibration summary.



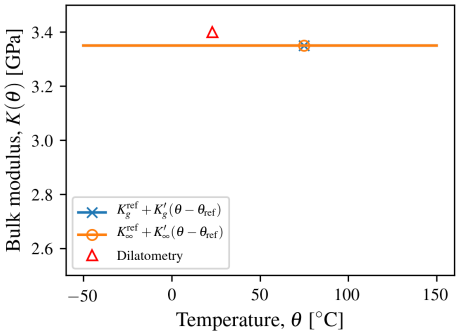
(a) WLF from shear master curve.



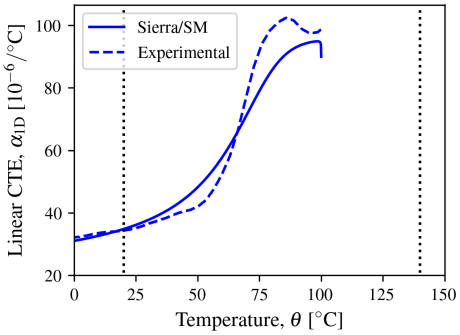
(b) Shear master curve



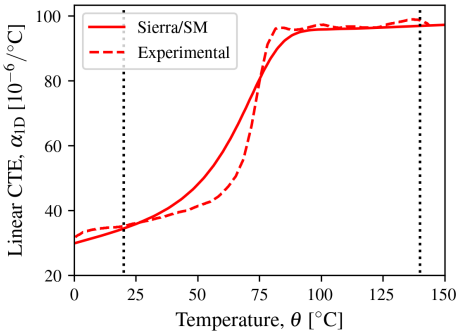
(c) Shear modulus vs. temperature



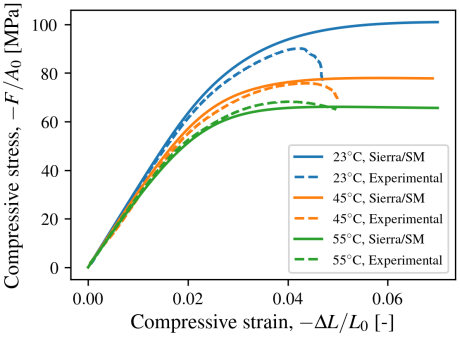
(d) Bulk modulus vs. temperature



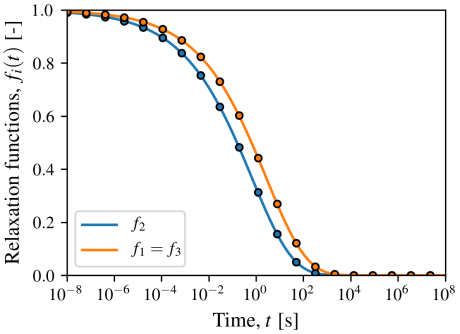
(e) CTE during cooling



(f) CTE during heating



(g) Uniaxial compression



(h) Relaxation functions

Figure 4-9. 828/DEA/GMB graphical summary for the legacy calibration in SAND2011-4751 [1].

5. MODEL CALIBRATION USING DEVELOPMENT FEATURES

The main development feature of SPECTACULAR is the inclusion of thermomechanical coupling by the addition of thermal terms in the Helmholtz free energy;

$$\begin{aligned}\Psi(t) = \Psi_\infty(\boldsymbol{\varepsilon},\theta) &+ \frac{1}{2}\left[K_g(\theta) - K_\infty(\theta)\right]\int_0^t\int_0^t f_1(t^*-s^*,t^*-u^*)\,\frac{\mathrm{d}I_1}{\mathrm{d}s}\frac{\mathrm{d}I_1}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u \\ &+ \left[G_g(\theta) - G_\infty(\theta)\right]\int_0^t\int_0^t f_2(t^*-s^*,t^*-u^*)\,\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}s}:\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u \\ &- \left[K_g(\theta)\,\delta_g(\theta) - K_\infty(\theta)\,\delta_\infty(\theta)\right]\int_0^t\int_0^t f_3(t^*-s^*,t^*-u^*)\,\frac{\mathrm{d}I_1}{\mathrm{d}s}\frac{\mathrm{d}\theta}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u \\ &- \frac{1}{2\theta_{\mathrm{ref}}}\left[C_g(\theta) - C_\infty(\theta)\right]\int_0^t\int_0^t f_4(t^*-s^*,t^*-u^*)\,\frac{\mathrm{d}\theta}{\mathrm{d}s}\frac{\mathrm{d}\theta}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u.\end{aligned} \tag{5.1}$$

Most of the terms in Eq. (5.1) were defined in Chapter 2, but new terms include f_4, the thermal relaxation function; $C_g(\theta)$, the glassy (constant strain) heat capacity; and $C_\infty(\theta)$, the rubbery (constant strain) heat capacity. Just like the other rubbery and glassy limits, the heat capacities are allowed to have a linear temperature dependence;

$$C_g(\theta) = C_g^{\mathrm{ref}} + C_g'(\theta - \theta_{\mathrm{ref}}), \qquad C_\infty(\theta) = C_\infty^{\mathrm{ref}} + C_\infty'(\theta - \theta_{\mathrm{ref}}). \tag{5.2}$$

Originally, the time-independent (equilibrium) contribution to the Helmholtz free energy was formulated in Ref. [10] as

$$\begin{aligned}\Psi_\infty(\boldsymbol{\varepsilon},\theta) = &\frac{K_\infty(\theta)}{2}I_1^2 + G_\infty(\theta)(\boldsymbol{e}:\boldsymbol{e}) - K_\infty(\theta)\,\delta_\infty(\theta)(\theta-\theta_{\mathrm{sf}})I_1 \\ &- C_\infty^{\mathrm{ref}}\theta\left[\ln\left(\frac{\theta}{\theta_{\mathrm{ref}}}\right) - 1\right] - C_\infty^{\mathrm{ref}}\theta_{\mathrm{ref}} - \frac{C_\infty'}{2}(\theta-\theta_{\mathrm{ref}})^2.\end{aligned} \tag{5.3}$$

However, the form in Eq. (5.3) led to undesirable behavior when calculating the heat capacity [5], specifically the product of C_∞' and the absolute temperature appear in the equation for the heat capacity.[1] This means that when parameterizing the heat capacity, the temperature dependence of the rubbery heat capacity could not be changed without also changing the heat capacity at all temperatures. Graphically, for a plot of heat capacity versus temperature, a change in the high temperature slope C_∞' also vertically shifted the entire curve. The problematic product of $C_\infty'\theta$ originated from the red terms in Eq. (5.3). To address this, a new form for the equilibrium heat capacity is proposed here:

$$\begin{aligned}\Psi_\infty(\boldsymbol{\varepsilon},\theta) = &\frac{K_\infty(\theta)}{2}I_1^2 + G_\infty(\theta)(\boldsymbol{e}:\boldsymbol{e}) - K_\infty(\theta)\,\delta_\infty(\theta)(\theta-\theta_{\mathrm{sf}})I_1 \\ &- \frac{C_\infty^{\mathrm{ref}}}{2\theta_{\mathrm{ref}}}(\theta-\theta_{\mathrm{ref}})^2 - \frac{C_\infty'}{6\theta_{\mathrm{ref}}}(\theta-\theta)^3.\end{aligned} \tag{5.4}$$

[1] Even a statement of the heat capacity equations would be too lengthy for inclusion here. See Ref. [10] for the development of the heat capacity equation.

The modified terms in Eq. (5.4) are written in blue. This new form eliminates the product $C'_\infty\theta$ from the heat capacity equation. This new form is also closer to the spirit of the original PEC model since the modified equilibrium terms are a Taylor series expansion about a reference state for changes in strain and temperature, while the non-equilibrium terms are a Frechet expansion (essentially a Taylor series for functionals) in the strain and temperature history. When performing the Coleman–Noll analysis on the free energy, thermal equilibrium terms pair with thermal non-equilibrium terms in a much cleaner way than for the previous free energy in Eq. (5.3). A redevelopment of the thermal equations using the new equilibrium free energy in Eq. (5.4) has not been formally documented, but can be obtained by following the same procedure in Ref. [10] using Eq. (5.4) instead of Eq. (5.4).

Another development feature of SPECTACULAR is related to the relaxation function associated with the thermal history in the clock. In PEC, the thermal relaxation function (f_4) controlled the effect of the temperature history on the shift factor. In SPEC, the thermal relaxation function was eliminated, and the volumetric relaxation function ($f_1 = f_3 = f_v$) was used instead. When SPECTACULAR re-introduced the ability to specify independent volumetric (f_1) and thermal-volumetric (f_3) relaxation functions, f_3 was then used to control the effect of the temperature history on the shift factor. Now that SPECTACULAR has also re-introduced the thermal relaxation function (f_4), model users can decide if f_3 or f_4 should be used in the shift factor definition. Therefore, the new equation for the material clock is

$$\begin{aligned} N = {} & \theta - \theta_{\text{ref}} - \int_0^t f_m\left(t^* - s^*\right) \frac{\mathrm{d}\theta}{\mathrm{d}s}\mathrm{d}s \\ & + C_3 \left(I_1 - I_{1,\text{ref}} - \int_0^t f_1\left(t^* - s^*\right) \frac{\mathrm{d}I_1}{\mathrm{d}s}\mathrm{d}s \right) \\ & + C_4 \int_0^t \int_0^t f_2\left(t^* - s^*, t^* - u^*\right) \frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}s} : \frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u, \\ m = {} & 3, 4. \end{aligned} \tag{5.5}$$

Studies in Ref. [5] indicate that using $m = 4$ (as with the original PEC model) may improve predictions of physical aging, especially yield stress evolution. Table 5-1 lists the model parameters required by the development features of SPECTACULAR.

The calibration using the development features of SPECTACULAR, henceforth referred to as the development calibration, will use the thermal relaxation function in the thermal hereditary integral in the material clock, i.e. $m = 4$. Changing which relaxation function is convoluted with the thermal history has broad implications for the material behavior, therefore parameters that were inferred from inverse identification using finite element simulations should be reevaluated. The development calibration procedure started with the parameters from the standard calibration (Table 4-11) but then parameters were updated following these steps:

1. The heat capacities (C_g^{ref}, C'_g, C_∞^{ref}, and C'_∞) and thermal relaxation function (f_4) were calibrated using the constant pressure heat capacity measured by a DSC during a stress-free temperature sweep. Inverse parameter identification was deployed where finite element simulations in Sierra/SM were used to iteratively evaluate the forward problem. For this calibration step, it was assumed that $f_1 = f_3 = f_4$. See Section 5.1.

Table 5-1. List of additional parameters for the development version of SPECTACULAR.

Parameter	Name in LAMÉ
C_g^{ref}	`heat capacity glassy 0`
C_g'	`heat capacity glassy 1`
C_∞^{ref}	`heat capacity rubbery 0`
C_∞'	`heat capacity rubbery 1`
m	`shift factor model`
τ_4 (thermal)	Not a direct input
β_4 (thermal)	Not a direct input

2. The glassy CTEs (α_g^{ref}, α_g') and the thermal strain relaxation function (f_3) were calibrated using the CTE measured by a TMA during a stress-free temperature sweep. Inverse parameter identification was deployed where finite element simulations in Sierra/SM were used to iteratively evaluate the forward problem. For this fitting step, as well as in the finalized development calibration, it was assumed that $f_1 = f_3$. See Section 5.2.

3. The shear strain clock parameter (C_4) was fit to stress–strain curves in glassy compression at three different temperatures. Inverse parameter identification was deployed where finite element simulations in Sierra/SM were used to iteratively evaluate the forward problem. See Section 5.3.

5.1. Heat capacity during a stress-free temperature sweep

The transition from the glassy heat capacity to the rubbery heat capacity measured by a DSC during a stress-free temperature sweep can be used to calibrate the thermal relaxation function (f_4) and the (constant strain) heat capacity parameters (C_g^{ref}, C_g', C_∞^{ref}, and C_∞'). Inverse methods deploying finite element simulations are needed to identify the parameters that best fit the experimental data. Mapping the simulated heat capacity onto the experimental measurements also requires the material density, since SPECTACULAR calculates the heat capacity per (current) volume while the experiments measure the heat capacity per mass.

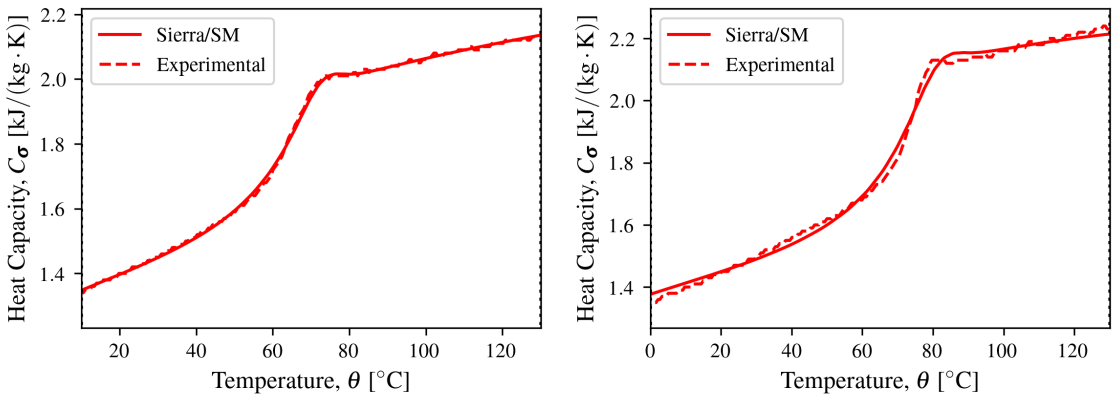
The temperature sweep in a DSC was simulated in Sierra/SM using a single element. The thermal history in the finite element simulation was designed to match the experiment as closely as possible. However, some information about the experimental procedures were missing on the Polymer Properties Database website. Unknown details of the experiments were assumed to match those reported in Ref. [4], which also describes work conducted by D.B. Adolf on filled epoxies. For 828/CTBN/DEA/GMB, the simulations start at 150 °C, cool to a 0 °C at a rate of 5 °C/min, hold at 0 °C for 5 min, and then reheat to 150 °C at 5 °C/min. For 828/DEA/GMB, the procedure is the same, except that the temperature is cooled to −10 °C.

Table 5-2. Development calibration parameters fit to the heat capacity during a stress-free temperature sweep for 828/CTBN/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times.

Parameter	Lower bound	Upper bound	Run 1	Run 2	Run 3 BEST	Units
$\log(\tau_4/\mathrm{s})$	-3	3	1.894	2.307	1.999	–
β_4	0.15	0.5	0.300	0.294	0.284	–
C_g^{ref}	1	2	1.153	1.142	1.156	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$
C_g'	-10	0	-1.785	-2.347	-1.783	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$
C_∞^{ref}	1	2	1.403	1.439	1.410	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$
C_∞'	-10	0	-2.134	-3.061	-2.270	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$
Objective			102	215	95	$\mathrm{J}/(\mathrm{kg}\cdot\mathrm{K})$

Table 5-3. Development calibration parameters fit to the heat capacity during a stress-free temperature sweep for 828/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times.

Parameter	Lower bound	Upper bound	Run 1	Run 2 BEST	Run 3	Units
$\log(\tau_4/\mathrm{s})$	-3	3	1.099	1.482	1.692	–
β_4	0.15	0.5	0.225	0.253	0.356	–
C_g^{ref}	1	2	1.083	1.122	1.249	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$
C_g'	-10	0	-2.628	-2.356	-0.954	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$
C_∞^{ref}	1	2	1.511	1.509	1.477	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$
C_∞'	-10	0	-2.552	-2.459	-1.614	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$
Objective			313	272	306	$\mathrm{J}/(\mathrm{kg}\cdot\mathrm{K})$



(a) 828/CTBN/DEA/GMB **(b) 828/DEA/GMB**

Figure 5-1. Heat capacity during a stress-free temperature sweep simulated by Sierra/SM. Parameters were optimized to fit the experimental data obtained from a differential scanning calorimeter (DSC). This fit is for the development calibration.

Six parameters were fit: all four heat capacity parameters (C_g^{ref}, C_g', C_∞^{ref}, and C_∞') and two parameters for the thermal relaxation function (τ_4, β_4). Since values for the characteristic time τ_4 can vary by orders of magnitude, the logarithm was optimized instead, $\log(\tau_4/\text{s})$. The parameter identification was conducted in Dakota using the `soga` method with a population size of 100 over 100 generations. The objective function was the L_2 norm of the absolute error between the (per mass) heat capacity during heating only. The L_2 norm only included data between 10 °C and 130 °C for 828/CTBN/DEA/GMB and between 0 °C and 130 °C for 828/DEA/GMB. To mitigate the risks of a bad random seed producing a sub-optimal fit, the `soga` method was repeated three times. The parameters identified from the heat capacity transition are shown in Tables 5-2 and 5-3. The resulting fit to the data is shown in Fig. 5-1.

5.2. Coefficient of thermal expansion during a stress-free temperature sweep

With a different relaxation function in the thermal hereditary integral of the clock, the CTE fit under a stress-free temperature sweep needs to be revisited. Most importantly, the thermal-volumetric relaxation function (f_3) should be re-calibrated. However, there are often differences between the apparent glassy CTE measured in experiments and the glassy CTE determined from inverse fitting. These differences depend on f_3, f_1 and potentially f_4 if it is integrated with the thermal history in the clock. Therefore, the glassy CTE parameters (α_g', α_g^{ref}) should also be re-calibrated if f_3 is changed and f_4 is placed in the clock definition. The rubbery CTE parameters typically match the apparent CTE measured by experiments. At high temperatures (low shift factors), the material response is not significantly affected by the relaxation functions, therefore the re-calibration of the rubbery CTE parameters is not necessary.

The CTE fitting step for the development calibration is essentially the same as for the standard

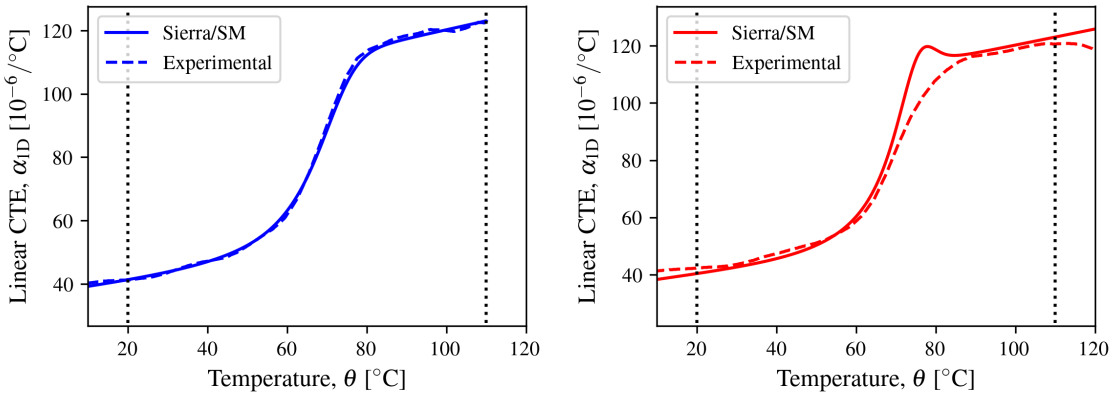
Table 5-4. Development calibration parameters fit to the CTE during a stress-free temperature sweep for 828/CTBN/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times.

Parameter	Lower bound	Upper bound	Run 1 BEST	Run 2	Run 3	Units
$\log(\tau_3/\mathrm{s})$	-2	4	3.175	3.224	3.136	–
β_3	0.15	0.5	0.358	0.378	0.333	–
α_g^{ref}	50	220	144	147	140	$10^{-6}/\mathrm{K}$
α_g'	0	1	0.5	0.6	0.3	$10^{-6}/\mathrm{K}^2$
Objective			150.1	151.3	150.7	$10^{-6}/\mathrm{K}$

Table 5-5. Development calibration parameters fit to the CTE during a stress-free temperature sweep for 828/DEA/GMB. The parameters were fit using the `soga` method in Dakota. The bounds used by the method are also listed. The method was executed three times.

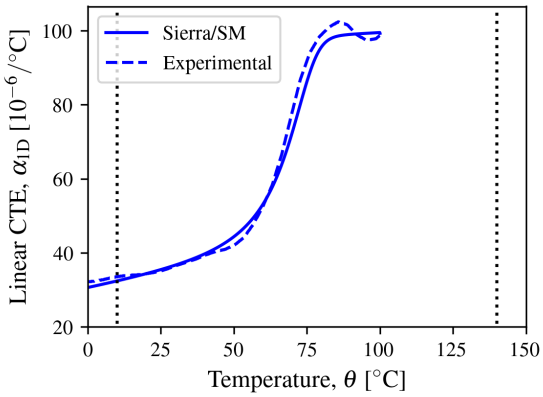
Parameter	Lower bound	Upper bound	Run 1	Run 2 BEST	Run 3	Units
$\log(\tau_3/\mathrm{s})$	-2	4	1.403	1.408	1.261	–
β_3	0.15	0.5	0.427	0.422	0.383	–
α_g^{ref}	50	220	116	115	104	$10^{-6}/\mathrm{K}$
α_g'	0	1	0.5	0.4	0.2	$10^{-6}/\mathrm{K}^2$
Objective			270.9	270.4	271.6	$10^{-6}/\mathrm{K}$

calibration in Section 4.4, with two exceptions. First, as previously mentioned, the rubbery CTE parameters were not re-calibrated. Second, the temperature range of the L_2 norm on the absolute error was expanded for 828/DEA/GMB from 20 °C–140 °C to 10 °C–140 °C. The parameters determined from the fit are listed in Tables 5-4 and 5-5. The finite element simulations for the best fits are compared to the experimental data in Fig. 5-2.

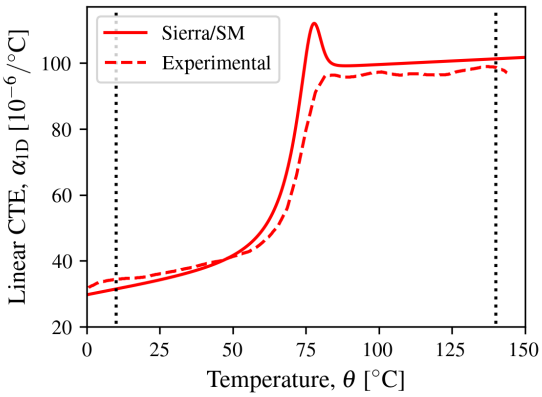


(a) 828/CTBN/DEA/GMB, Cool

(b) 828/CTBN/DEA/GMB, Heat



(c) 828/DEA/GMB, Cool



(d) 828/DEA/GMB, Heat

Figure 5-2. Coefficient of thermal expansion (CTE) during a stress-free temperature sweep simulated by Sierra/SM. Parameters were optimized to fit the experimental data obtained from a thermomechanical analyzer (TMA). This fit is for the development calibration.

5.3. Glassy compression

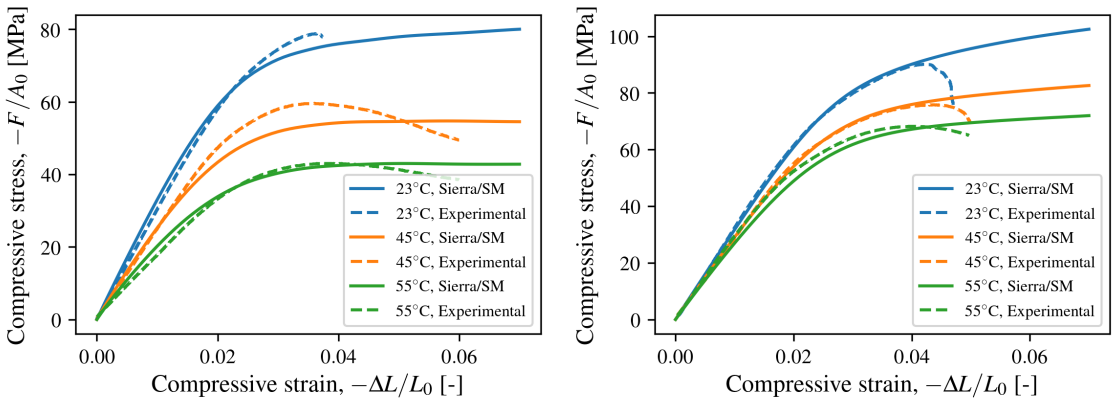
Finally, the parameter controlling the effect of shear strain on the shift factor (C_4) should be re-calibrated for the new thermal relaxation function. As with the standard calibration, this parameter is calibrated using the yield stress in glassy compression. This fitting step uses the same procedure as in Section 4.5 with one modification. In the standard calibration, 828/CTBN/DEA/GMB used a genetic algorithm where the glassy shear modulus parameters were also calibrated. Without adjusting the glassy shear modulus, the glassy Young's modulus in compression was not well matched to experiments. The same G'_g and G_g^{ref} from the standard calibration gave a satisfactory match to the glassy Young's modulus in the development calibration and therefore were not updated. With only one parameter to match, a genetic algorithm is unnecessary, so C_4 for 828/CTBN/DEA/GMB was fit using a gradient algorithm `conmin_frcg`, just like 828/DEA/GMB in the standard calibration. The best fit C_4 parameters are shown in Tables 5-6 and 5-7. The stress–strain curves for the best fit are shown in Fig. 5-3.

Table 5-6. Development calibration parameters fit to glassy compression at three different temperatures for 828/CTBN/DEA/GMB. The parameters were fit using the `conmin_frcg` method in Dakota. The bounds and initial point used by the method are also listed.

Parameter	Lower bound	Upper bound	Initial point	Result	Units
C_4	0	100000	20000	18200	K

Table 5-7. Development calibration parameters fit to glassy compression at three different temperatures for 828/DEA/GMB. The parameters were fit using the `conmin_frcg` method in Dakota. The bounds and initial point used by the method are also listed.

Parameter	Lower bound	Upper bound	Initial point	Result	Units
C_4	0	100000	50000	12900	K



(a) 828/CTBN/DEA/GMB **(b) 828/DEA/GMB**

Figure 5-3. Stress–strain response under glassy uniaxial compression simulated by Sierra/SM. Parameters were optimized to fit the experimental data at loading temperatures of 23 °C, 45 °C, **and** 55 °C**. This fit is for the development calibration.**

5.4. Calibrated parameters

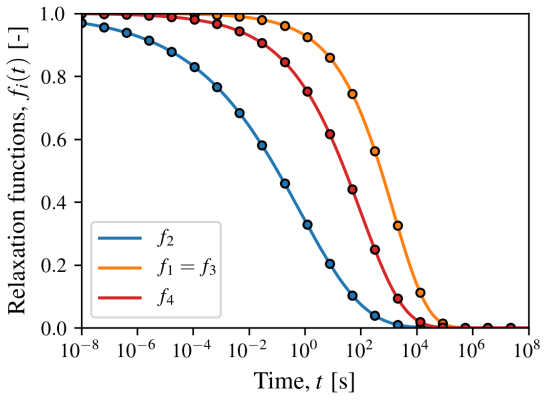
The final parameters for the development calibration are listed in Table 5-8. Parameters not listed in Table 5-8 are unchanged from the standard calibration and therefore can be found in Table 4-11. Graphical calibration summaries for 828/CTBN/DEA/GMB and 828/DEA/GMB can be found in Figs. 5-4 and 5-5, repsectively. These calibration summaries include fits to experimental data and plots of relaxation functions. For the plots of the relaxation functions, Figs. 5-4a and 5-5a, the Prony series actually used in the model are plotted with solid lines and compared to the stretched exponential parameters listed in Table 5-8, which are plotted with circles. In the standard calibration, several parameters were calibrated from explicit analyses that did not involve f_4 (WLF parameters, shear master curve, isofrequency temperature sweep, bulk modulus composite analysis). These analyses are unchanged from the standard calibration and therefore are not included in the graphical development calibration summaries. The complete material definitions for use with Sierra/SM are given in Appendices D and E for 828/CTBN/DEA/GMB and 828/DEA/GMB, respectively.

The heat capacity fits in the calibration summaries (Figs. 5-4b and 5-5b) are slightly broader than the fit from the first development calibration step seen in Fig. 5-1. This is due to modest coupling between the constant stress heat capacity and the thermal strain and the fact the second development calibration step (Section 5.2) updated f_3 and $\alpha_g(\theta)$. However, even the modified heat capacity fit matches the experimental data reasonably well. For more information on the coupling between the heat capacity and the thermal strain, refer to Figs. 2-5, 2-6, and 2-7 in Ref. [5].

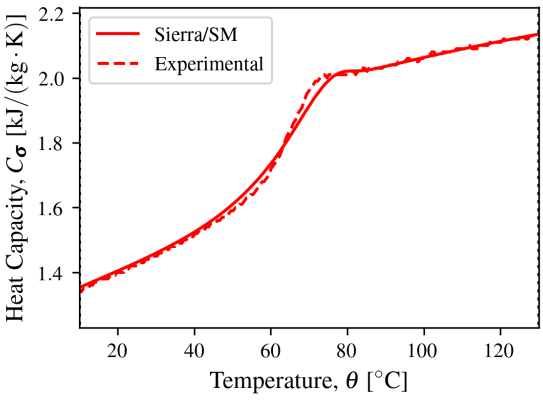
Notice that the glassy CTE parameters G_g^{ref} and G_g' are significantly different between the standard and development calibrations. For example value of G_g' increased by 27 % for 828/CTBN/DEA/GMB and 37 % for 828/DEA/GMB. This illustrates the fact that the apparent glassy CTE is not always the same as the (true, instantaneous) CTE that must be input into the model, and that the difference between the apparent glassy and true glassy CTE depends on f_3, f_1, and whichever relaxation function is used in the clock thermal hereditary integral (either f_3 or f_4).

Table 5-8. Calibrated development parameters for 828/CTBN/DEA/GMB and 828/DEA/GMB. Only parameters that have changed from those in Table 4-11 are listed here.

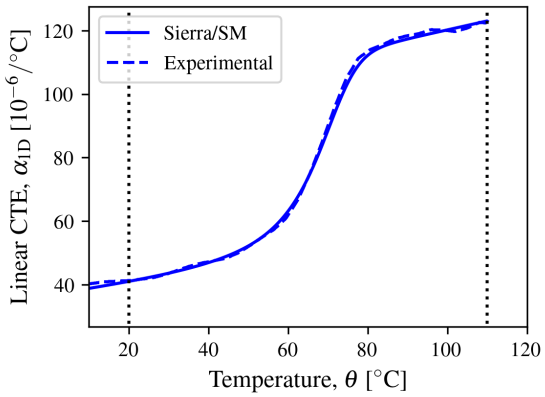
Parameter	828/CTBN/DEA/GMB	828/DEA/GMB	Units
α_g^{ref}	144	115	$10^{-6}/\text{K}$
α_g'	0.5	0.4	$10^{-6}/\text{K}^2$
C_g^{ref}	1.156	1.122	$\text{MJ}/(\text{m}^3\cdot\text{K})$
C_g'	-1.783	-2.356	$\text{kJ}/(\text{m}^3\cdot\text{K}^2)$
C_∞^{ref}	1.410	1.509	$\text{MJ}/(\text{m}^3\cdot\text{K})$
C_∞'	-2.270	-2.459	$\text{kJ}/(\text{m}^3\cdot\text{K}^2)$
C_4	18 200	12 900	K
m	4	4	–
$\tau_1 = \tau_3$ (volume)	1496	25.6	s
$\beta_1 = \beta_3$ (volume)	0.358	0.422	–
τ_4 (thermal)	99.8	30.3	s
β_4 (thermal)	0.284	0.253	–



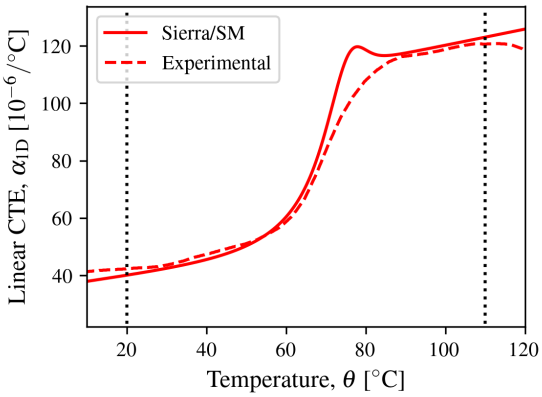
(a) Relaxation functions



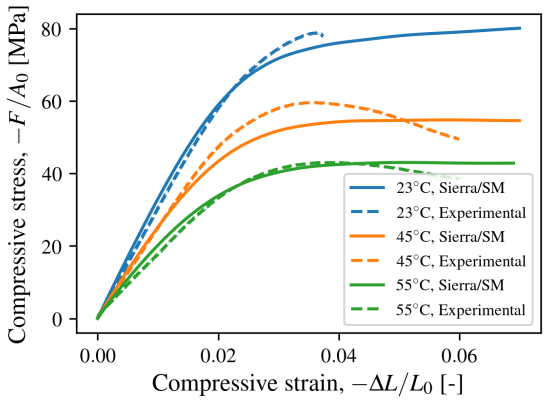
(b) Heat capacity



(c) CTE during cooling

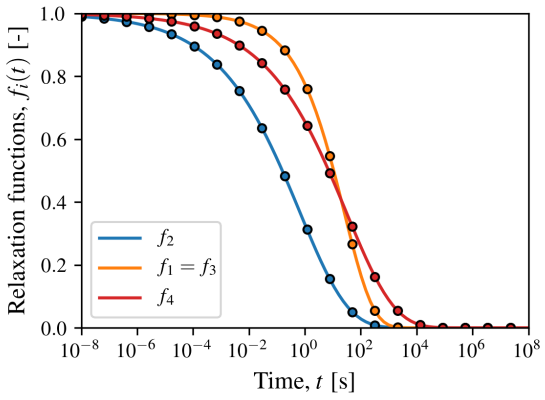


(d) CTE during heating

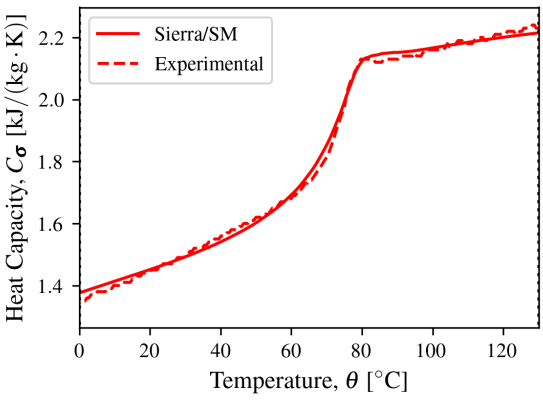


(e) Uniaxial compression

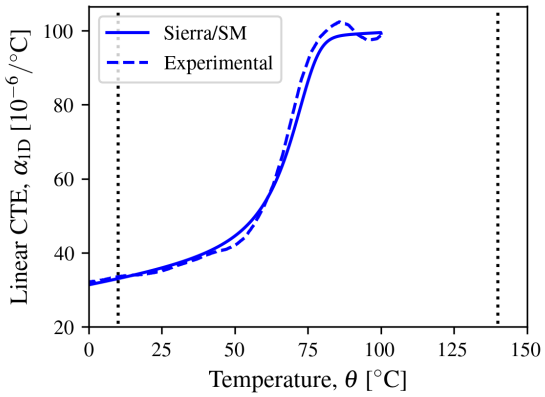
Figure 5-4. 828/CTBN/DEA/GMB graphical summary for the development calibration.



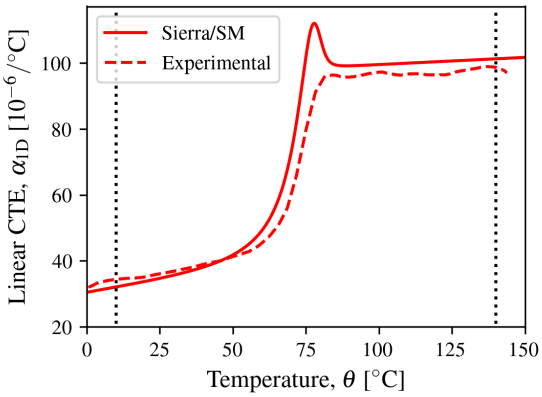
(a) Relaxation functions



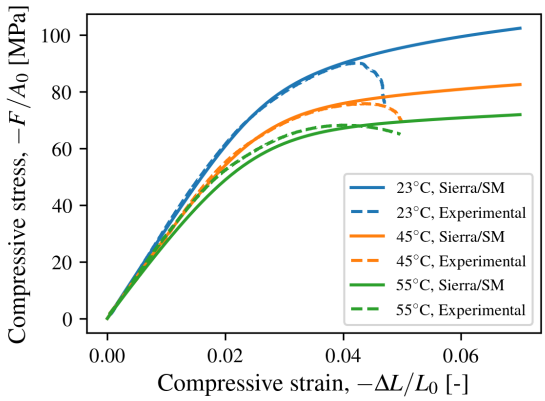
(b) Heat capacity



(c) CTE during cooling



(d) CTE during heating



(e) Uniaxial compression

Figure 5-5. 828/DEA/GMB graphical summary for the development calibration.

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APPENDIX A. Sierra/SM material definition for 828/CTBN/DEA/GMB: Standard SPECTACULAR calibration

```
# File: 828_ctbn_dea_gmb_sand2022-6360_table4-11.txt
#
# Material: 828/CTBN/DEA/GMB
# Calibration: SAND2022-6360, Table 4-11
#
# 2022-02
# Ken Cundiff (kcundif@sandia.gov)
# Calibrated from data on Polymer Properties Database website
#
# NOTE: Set stress free-temperature based on application
#
# --- Material Information from Polymer Properties Database
   website ---
#
# 100 pbw adduct of digylcidyl ether of bisphenol A (Epon 828)
   and Hycar
#  1300x8 carboxyl terminated butadine acrylonitrile rubber (CTBN
   )
# 12 pbw diethanolamine
# 28 pbw 3M D32 glass microbaloons (48% by volume)
# Cured 24 hours at 71 C

begin material 828_ctbn_dea_gmb

   density = 770 # kg/m^3
   thermal log strain function = sierra_constant_function_zero

   begin parameters for model spectacular
      bulk modulus      = 3.1E9     # Pa
      shear modulus     = 1.089E9   # Pa
      bulk glassy 0     = 3.1E9     # Pa
      bulk glassy 1     = -3.3E6    # Pa/K
      bulk rubbery 0    = 2.5E9     # Pa
      bulk rubbery 1    = -3.5E6    # Pa/K
      shear glassy 0    = 1.089E9   # Pa
      shear glassy 1    = -9.2E6    # Pa/K
```

```
shear rubbery 0   = 20E6      # Pa
shear rubbery 1   = 0         # Pa/K
volcte glassy 0   = 113E-6    # K^-1
volcte glassy 1   = 0         # K^-2
volcte rubbery 0  = 333E-6    # K^-1
volcte rubbery 1  = 0.8E-6    # K^-2
# heat capacity not used
heat capacity glassy 0 = 1    # J/(m^3*K)
heat capacity glassy 1 = 0    # J/(m^3*K^2)
heat capacity rubbery 0 = 1   # J/(m^3*K)
heat capacity rubbery 1 = 0   # J/(m^3*K^2)
reference temperature = 338   # K
wlf c1            = 14.9      # None
wlf c2            = 53.4      # K
clock c1          = 0         # None
clock c2          = 0         # K
clock c3          = 1000      # K
clock c4          = 14600     # K
stress free temperature = {stress_free_temperature} # K
# === NOT IMPLEMNTED OR UNDER DEVELOPMENT ===
bulk glassy 2     = 0
bulk rubbery 2    = 0
shear glassy 2    = 0
shear rubbery 2   = 0
volcte glassy 2   = 0
volcte rubbery 2  = 0
clock c5          = 0
clock c6          = 0
#Tmatch_wlf_arh    = -2929
#EACT_ON_R         = 60493.08479

#RELAX_TIMEi terms have units of s
#Fi terms are unitless

# Spectrum ID = 1
##KWW Relaxation Function with
##KWW_tau = 1.606086e+03, KWW_beta = 2.676130e-01
##and 29 prony terms in use
##Prony L2 Projection Error = 1.873967e-04
##
RELAX_TIME1 = 3.09775536e-08 9.67674763e-08 3.02281600e-07
   9.44265254e-07 2.94968953e-06 9.21422057e-06 2.87833210e
   -05 8.99131470e-05 2.80870092e-04 8.77380127e-04
   2.74075421e-03 8.56154981e-03 2.67445124e-02 8.35443304e
   -02 2.60975224e-01 8.15232673e-01 2.54661841e+00
```

```
   7.95510967e+00 2.48501188e+01 7.76266360e+01 2.42489570e
   +02 7.57487308e+02 2.36623382e+03 7.39162550e+03
   2.30899107e+04 7.21281096e+04 2.25313310e+05 7.03832220e
   +05 2.19862642e+06
F1 = 4.22554108e-04 4.86381536e-04 5.49252344e-04
   8.69075415e-04 1.08808328e-03 1.53157544e-03 2.03926649e
   -03 2.78177192e-03 3.75029255e-03 5.07593056e-03
   6.84633950e-03 9.22654184e-03 1.23990551e-02 1.66099186e
   -02 2.21490455e-02 2.93516155e-02 3.85656286e-02
   5.00698236e-02 6.39446971e-02 7.97786242e-02 9.63311766e
   -02 1.10950699e-01 1.19448697e-01 1.16403779e-01
   9.81331512e-02 6.64453163e-02 3.27119451e-02 9.64376229e
   -03 1.56523776e-03

# Spectrum ID = 2
##KWW Relaxation Function with
##KWW_tau = 6.946172e-01, KWW_beta = 1.919384e-01
##and 30 prony terms in use
##Prony L2 Projection Error = 1.222320e-03
##
RELAX_TIME2 = 1.63253383e-16 7.99062171e-16 3.91110030e-15
   1.91433234e-14 9.36991645e-14 4.58621173e-13 2.24477328e
   -12 1.09872971e-11 5.37785699e-11 2.63225301e-10
   1.28838605e-09 6.30615145e-09 3.08661725e-08 1.51077977e
   -07 7.39468271e-07 3.61941120e-06 1.77156181e-05
   8.67110992e-05 4.24417296e-04 2.07735853e-03 1.01678666e
   -02 4.97677746e-02 2.43594010e-01 1.19229847e+00
   5.83583991e+00 2.85641794e+01 1.39810611e+02 6.84318872e
   +02 3.34947623e+03 1.63943908e+04
F2 = 1.90342700e-05 5.29126359e-04 3.91278848e-04
   7.05610400e-04 8.66738677e-04 1.21985325e-03 1.62957378e
   -03 2.21795091e-03 2.99539529e-03 4.05264588e-03
   5.47127803e-03 7.37759811e-03 9.92546067e-03 1.33151325e
   -02 1.77914540e-02 2.36451333e-02 3.11944748e-02
   4.07438674e-02 5.24904380e-02 6.63636828e-02 8.17535017e
   -02 9.71715250e-02 1.09872796e-01 1.15894265e-01
   1.10789987e-01 9.22395188e-02 6.28614634e-02 3.24415595e
   -02 1.07697466e-02 2.38442661e-03

# Spectrum ID = 3
##KWW Relaxation Function with
##KWW_tau = 1.606086e+03, KWW_beta = 2.676130e-01
##and 29 prony terms in use
##Prony L2 Projection Error = 1.873967e-04
##
```

```
RELAX_TIME3 = 3.09775536e-08 9.67674763e-08 3.02281600e-07
   9.44265254e-07 2.94968953e-06 9.21422057e-06 2.87833210e
   -05 8.99131470e-05 2.80870092e-04 8.77380127e-04
   2.74075421e-03 8.56154981e-03 2.67445124e-02 8.35443304e
   -02 2.60975224e-01 8.15232673e-01 2.54661841e+00
   7.95510967e+00 2.48501188e+01 7.76266360e+01 2.42489570e
   +02 7.57487308e+02 2.36623382e+03 7.39162550e+03
   2.30899107e+04 7.21281096e+04 2.25313310e+05 7.03832220e
   +05 2.19862642e+06
F3 = 4.22554108e-04 4.86381536e-04 5.49252344e-04
   8.69075415e-04 1.08808328e-03 1.53157544e-03 2.03926649e
   -03 2.78177192e-03 3.75029255e-03 5.07593056e-03
   6.84633950e-03 9.22654184e-03 1.23990551e-02 1.66099186e
   -02 2.21490455e-02 2.93516155e-02 3.85656286e-02
   5.00698236e-02 6.39446971e-02 7.97786242e-02 9.63311766e
   -02 1.10950699e-01 1.19448697e-01 1.16403779e-01
   9.81331512e-02 6.64453163e-02 3.27119451e-02 9.64376229e
   -03 1.56523776e-03

# Spectrum ID = 4
##KWW Relaxation Function with
##KWW_tau = 1.606086e+03, KWW_beta = 2.676130e-01
##and 29 prony terms in use
##Prony L2 Projection Error = 1.873967e-04
##
RELAX_TIME4 = 3.09775536e-08 9.67674763e-08 3.02281600e-07
   9.44265254e-07 2.94968953e-06 9.21422057e-06 2.87833210e
   -05 8.99131470e-05 2.80870092e-04 8.77380127e-04
   2.74075421e-03 8.56154981e-03 2.67445124e-02 8.35443304e
   -02 2.60975224e-01 8.15232673e-01 2.54661841e+00
   7.95510967e+00 2.48501188e+01 7.76266360e+01 2.42489570e
   +02 7.57487308e+02 2.36623382e+03 7.39162550e+03
   2.30899107e+04 7.21281096e+04 2.25313310e+05 7.03832220e
   +05 2.19862642e+06
F4 = 4.22554108e-04 4.86381536e-04 5.49252344e-04
   8.69075415e-04 1.08808328e-03 1.53157544e-03 2.03926649e
   -03 2.78177192e-03 3.75029255e-03 5.07593056e-03
   6.84633950e-03 9.22654184e-03 1.23990551e-02 1.66099186e
   -02 2.21490455e-02 2.93516155e-02 3.85656286e-02
   5.00698236e-02 6.39446971e-02 7.97786242e-02 9.63311766e
   -02 1.10950699e-01 1.19448697e-01 1.16403779e-01
   9.81331512e-02 6.64453163e-02 3.27119451e-02 9.64376229e
   -03 1.56523776e-03
```

```
   end parameters for model spectacular

end material 828_ctbn_dea_gmb
```

APPENDIX B. Sierra/SM material definition for 828/DEA/GMB: Standard SPECTACULAR calibration

```
# File: 828_dea_gmb_sand2022-6360_table4-11.txt
#
# Material: 828/DEA/GMB
# Calibration: SAND2022-6360, Table 4-11
#
# 2022-02
# Ken Cundiff (kcundif@sandia.gov)
# Calibrated from data on Polymer Properties Database website
#
# NOTE: Set stress free-temperature based on application
#
# --- Material Information from Polymer Properties Database
   website ---
#
# 100 pbw adduct of digylcidyl ether of bisphenol A (Epon 828)
# 12 pbw diethanolamine
# 28 pbw 3M D32 glass microbaloons (48% by volume)
# Cured 24 hours at 71 C

begin material 828_dea_gmb

   density = 760 # kg/m^3
   thermal log strain function = sierra_constant_function_zero

   begin parameters for model spectacular
      bulk modulus      = 3.2E9     # Pa
      shear modulus     = 1.118E9   # Pa
      bulk glassy 0     = 3.2E9     # Pa
      bulk glassy 1     = -3.7E6    # Pa/K
      bulk rubbery 0    = 2.6E9     # Pa
      bulk rubbery 1    = -3.9E6    # Pa/K
      shear glassy 0    = 1.118E9   # Pa
      shear glassy 1    = -2E6      # Pa/K
      shear rubbery 0   = 40E6      # Pa
      shear rubbery 1   = 0         # Pa/K
      volcte glassy 0   = 84E-6     # K^-1
```

```
volcte glassy 1   = 0          # K^-2
volcte rubbery 0  = 296E-6     # K^-1
volcte rubbery 1  = 0.1E-06    # K^-2
# heat capacity not used
heat capacity glassy 0 = 1     # J/(m^3*K)
heat capacity glassy 1 = 0     # J/(m^3*K^2)
heat capacity rubbery 0 = 1    # J/(m^3*K)
heat capacity rubbery 1 = 0    # J/(m^3*K^2)
reference temperature = 348    # K
wlf c1            = 13.8       # None
wlf c2            = 53.9       # K
clock c1          = 0          # None
clock c2          = 0          # K
clock c3          = 1000       # K
clock c4          = 19600      # K
stress free temperature = {stress_free_temperature} # K
# === NOT IMPLEMNTED OR UNDER DEVELOPMENT ===
bulk glassy 2     = 0
bulk rubbery 2    = 0
shear glassy 2    = 0
shear rubbery 2   = 0
volcte glassy 2   = 0
volcte rubbery 2  = 0
clock c5          = 0
clock c6          = 0
#Tmatch_wlf_arh    = -2929
#EACT_ON_R         = 60493.08479

#RELAX_TIMEi terms have units of s
#Fi terms are unitless

# Spectrum ID = 1
##KWW Relaxation Function with
##KWW_tau = 2.681435e+00, KWW_beta = 2.559214e-01
##and 29 prony terms in use
##Prony L2 Projection Error = 2.254295e-04
##
RELAX_TIME1 = 1.67551902e-11 5.51354538e-11 1.81431438e-10
   5.97027223e-10 1.96460717e-09 6.46483306e-09 2.12734979e
   -08 7.00036195e-08 2.30357356e-07 7.58025256e-07
   2.49439522e-06 8.20817971e-06 2.70102402e-05 8.88812261e
   -05 2.92476938e-04 9.62439010e-04 3.16704918e-03
   1.04216479e-02 3.42939878e-02 1.12849484e-01 3.71348068e
   -01 1.22197623e+00 4.02109515e+00 1.32320136e+01
   4.35419155e+01 1.43281170e+02 4.71488073e+02 1.55150186e
```

```
   +03 5.10544840e+03
F1 = 4.55093124e-04 4.45683522e-04 5.98553603e-04
   8.50809838e-04 1.12125058e-03 1.53969544e-03 2.07283111e
   -03 2.81317172e-03 3.80080430e-03 5.13843390e-03
   6.93254907e-03 9.33862185e-03 1.25467647e-02 1.67999302e
   -02 2.23898656e-02 2.96479257e-02 3.89155179e-02
   5.04574641e-02 6.43294625e-02 8.00860975e-02 9.64459551e
   -02 1.10739709e-01 1.18822430e-01 1.15438842e-01
   9.71609002e-02 6.59108679e-02 3.27739259e-02 9.88434757e
   -03 1.70497552e-03

# Spectrum ID = 2 (shear)
##KWW Relaxation Function with
##KWW_tau = 6.612664e-01, KWW_beta = 2.529541e-01
##and 29 prony terms in use
##Prony L2 Projection Error = 2.389765e-04
##
RELAX_TIME2 = 3.05300475e-12 1.01877210e-11 3.39959052e-11
   1.13442601e-10 3.78552169e-10 1.26320927e-09 4.21526487e
   -09 1.40661238e-08 4.69379371e-08 1.56629501e-07
   5.22664651e-07 1.74410527e-06 5.81999027e-06 1.94210105e
   -05 6.48069209e-05 2.16257388e-04 7.21639867e-04
   2.40807541e-03 8.03562475e-03 2.68144697e-02 8.94785169e
   -02 2.98585245e-01 9.96363723e-01 3.32481490e+00
   1.10947376e+01 3.70225733e+01 1.23542438e+02 4.12254810e
   +02 1.37567326e+03
F2 = 4.62643796e-04 4.36947952e-04 6.09271260e-04
   8.47591092e-04 1.12860831e-03 1.54240300e-03 2.08083521e
   -03 2.82135316e-03 3.81332549e-03 5.15427037e-03
   6.95415598e-03 9.36685561e-03 1.25838808e-02 1.68477315e
   -02 2.24504120e-02 2.97224485e-02 3.90035131e-02
   5.05550128e-02 6.44264009e-02 8.01639255e-02 9.64758944e
   -02 1.10688806e-01 1.18668181e-01 1.15200027e-01
   9.69179484e-02 6.57737816e-02 3.27830960e-02 9.94133463e
   -03 1.74010061e-03

# Spectrum ID = 3
##KWW Relaxation Function with
##KWW_tau = 2.681435e+00, KWW_beta = 2.559214e-01
##and 29 prony terms in use
##Prony L2 Projection Error = 2.254295e-04
##
RELAX_TIME3 = 1.67551902e-11 5.51354538e-11 1.81431438e-10
   5.97027223e-10 1.96460717e-09 6.46483306e-09 2.12734979e
   -08 7.00036195e-08 2.30357356e-07 7.58025256e-07
```

```
      2.49439522e-06 8.20817971e-06 2.70102402e-05 8.88812261e
      -05 2.92476938e-04 9.62439010e-04 3.16704918e-03
      1.04216479e-02 3.42939878e-02 1.12849484e-01 3.71348068e
      -01 1.22197623e+00 4.02109515e+00 1.32320136e+01
      4.35419155e+01 1.43281170e+02 4.71488073e+02 1.55150186e
      +03 5.10544840e+03
   F3 = 4.55093124e-04 4.45683522e-04 5.98553603e-04
      8.50809838e-04 1.12125058e-03 1.53969544e-03 2.07283111e
      -03 2.81317172e-03 3.80080430e-03 5.13843390e-03
      6.93254907e-03 9.33862185e-03 1.25467647e-02 1.67999302e
      -02 2.23898656e-02 2.96479257e-02 3.89155179e-02
      5.04574641e-02 6.43294625e-02 8.00860975e-02 9.64459551e
      -02 1.10739709e-01 1.18822430e-01 1.15438842e-01
      9.71609002e-02 6.59108679e-02 3.27739259e-02 9.88434757e
      -03 1.70497552e-03

   # Spectrum ID = 4
   ##KWW Relaxation Function with
   ##KWW_tau = 2.681435e+00, KWW_beta = 2.559214e-01
   ##and 29 prony terms in use
   ##Prony L2 Projection Error = 2.254295e-04
   ##
   RELAX_TIME4 = 1.67551902e-11 5.51354538e-11 1.81431438e-10
      5.97027223e-10 1.96460717e-09 6.46483306e-09 2.12734979e
      -08 7.00036195e-08 2.30357356e-07 7.58025256e-07
      2.49439522e-06 8.20817971e-06 2.70102402e-05 8.88812261e
      -05 2.92476938e-04 9.62439010e-04 3.16704918e-03
      1.04216479e-02 3.42939878e-02 1.12849484e-01 3.71348068e
      -01 1.22197623e+00 4.02109515e+00 1.32320136e+01
      4.35419155e+01 1.43281170e+02 4.71488073e+02 1.55150186e
      +03 5.10544840e+03
   F4 = 4.55093124e-04 4.45683522e-04 5.98553603e-04
      8.50809838e-04 1.12125058e-03 1.53969544e-03 2.07283111e
      -03 2.81317172e-03 3.80080430e-03 5.13843390e-03
      6.93254907e-03 9.33862185e-03 1.25467647e-02 1.67999302e
      -02 2.23898656e-02 2.96479257e-02 3.89155179e-02
      5.04574641e-02 6.43294625e-02 8.00860975e-02 9.64459551e
      -02 1.10739709e-01 1.18822430e-01 1.15438842e-01
      9.71609002e-02 6.59108679e-02 3.27739259e-02 9.88434757e
      -03 1.70497552e-03

end parameters for model spectacular

end material 828_dea_gmb
```

APPENDIX C. Sierra/SM material definition for 828/DEA/GMB: SPECTACULAR calibration using parameters from SAND2011-4751

```
# File: 828_dea_gmb_sand2011-4751.txt
#
# Material: 828/DEA/GMB
# Calibration: SAND2011-4751
#
# NOTE: Set stress free-temperature based on application
#
# --- Material Information from Polymer Properties Database
   website ---
# Composition of material reported in Section 2.1.1 of report,
   but its less
# detailed than the Polymer Properties Database.
#
# 100 pbw adduct of digylcidyl ether of bisphenol A (Epon 828)
# 12 pbw diethanolamine
# 28 pbw 3M D32 glass microbaloons (48% by volume)
# Cured 24 hours at 71 C

begin property specification for material 828_dea_gmb

   density = 750 # kg/m^3
   thermal log strain function = sierra_constant_function_zero

   begin parameters for model spectacular
      bulk modulus      = 3.35E9    # Pa
      shear modulus     = 1.2E9     # Pa
      bulk glassy 0     = 3.35E9    # Pa
      bulk glassy 1     = 0         # Pa/K
      bulk rubbery 0    = 3.35E9    # Pa
      bulk rubbery 1    = 0         # Pa/K
      shear glassy 0    = 1.2E9     # Pa
      shear glassy 1    = -1E6      # Pa/K
      shear rubbery 0   = 40E6      # Pa
      shear rubbery 1   = 0         # Pa/K
      volcte glassy 0   = 81E-6     # K^-1
```

```
volcte glassy 1   = 0.1E-6    # K^-2
volcte rubbery 0  = 285E-6    # K^-1
volcte rubbery 1  = 0.07E-06  # K^-2
# heat capacity not used
heat capacity glassy 0 = 1    # J/(m^3*K)
heat capacity glassy 1 = 0    # J/(m^3*K^2)
heat capacity rubbery 0 = 1   # J/(m^3*K)
heat capacity rubbery 1 = 0   # J/(m^3*K^2)
reference temperature = 348   # K
wlf c1            = 12.5      # None
wlf c2            = 45.4      # K
clock c1          = 0         # None
clock c2          = 0         # K
clock c3          = 1000      # K

# C3=2000 in the report. Notes in Kevin Long's copy
   indicate 2000 may
# be a typo and 1000 was actually used.

clock c4          = 17500     # K
stress free temperature = {stress_free_temperature} # K
# === NOT IMPLEMNTED OR UNDER DEVELOPMENT ===
bulk glassy 2     = 0
bulk rubbery 2    = 0
shear glassy 2    = 0
shear rubbery 2   = 0
volcte glassy 2   = 0
volcte rubbery 2  = 0
clock c5          = 0
clock c6          = 0

#RELAX_TIMEi terms have units of s
#Fi terms are unitless

# Spectrum ID = 1
##KWW Relaxation Function with
##KWW_tau = 2.000000e+01, KWW_beta = 1.500000e-01
##and 48 prony terms in use
##Prony L2 Projection Error = 1.767624e-04
##
RELAX_TIME1 = 6.84998022e-19 2.33830085e-18 7.98199512e-18
   2.72472407e-17 9.30108469e-17 3.17500687e-16 1.08381645e
   -15 3.69970255e-15 1.26292593e-14 4.31110847e-14
   1.47163470e-13 5.02355418e-13 1.71483430e-12 5.85373733e
   -12 1.99822460e-11 6.82111499e-11 2.32844745e-10
```

```
   7.94835968e-10 2.71324232e-09 9.26189071e-09 3.16162766e
   -08 1.07924934e-07 3.68411232e-07 1.25760407e-06
   4.29294182e-06 1.46543336e-05 5.00238535e-05 1.70760813e
   -04 5.82907018e-04 1.98980425e-03 6.79237140e-03
   2.31863557e-02 7.91486597e-02 2.70180895e-01 9.22286190e
   -01 3.14830483e+00 1.07470148e+01 3.66858779e+01
   1.25230463e+02 4.27485173e+02 1.45925815e+03 4.98130572e
   +03 1.70041242e+04 5.80450698e+04 1.98141939e+05
   6.76374893e+05 2.30886504e+06 7.88151340e+06
F1 = 3.18457650e-04 1.86938527e-04 3.10489826e-04
   3.33676491e-04 4.21468277e-04 4.95118502e-04 6.01404460e
   -04 7.18830255e-04 8.65690264e-04 1.03855044e-03
   1.24791649e-03 1.49787231e-03 1.79815900e-03 2.15752484e
   -03 2.58796371e-03 3.10269763e-03 3.71782332e-03
   4.45187248e-03 5.32658985e-03 6.36699094e-03 7.60175031e
   -03 9.06325319e-03 1.07875231e-02 1.28137970e-02
   1.51834846e-02 1.79385468e-02 2.11183988e-02 2.47559774e
   -02 2.88706854e-02 3.34609029e-02 3.84902051e-02
   4.38766612e-02 4.94694209e-02 5.50425048e-02 6.02605683e
   -02 6.47068618e-02 6.78369714e-02 6.91207509e-02
   6.79495189e-02 6.40617228e-02 5.71802564e-02 4.80551299e
   -02 3.69798578e-02 2.63566562e-02 1.57948677e-02
   9.47733572e-03 2.83252334e-03 2.46653735e-03

# Spectrum ID = 2
##KWW Relaxation Function with
##KWW_tau = 5.100000e-01, KWW_beta = 2.310000e-01
##and 46 prony terms in use
##Prony L2 Projection Error = 1.191934e-04
##
RELAX_TIME2 = 1.16879560e-13 5.75732143e-13 2.83597492e-12
   6.29424061e-12 1.39696104e-11 3.10045370e-11 6.88123207e
   -11 1.52723954e-10 3.38959737e-10 7.52296547e-10
   1.66966761e-09 3.70570615e-09 8.22454598e-09 1.82537832e
   -08 4.05129476e-08 8.99155483e-08 1.99561037e-07
   4.42911245e-07 9.83009378e-07 2.18171800e-06 4.84216484e
   -06 1.07468336e-05 2.38518176e-05 5.29373789e-05
   1.17490672e-04 2.60762024e-04 5.78742397e-04 1.28447677e
   -03 2.85080300e-03 6.32715047e-03 1.40426515e-02
   3.11666463e-02 6.91721105e-02 1.53522481e-01 3.40732011e
   -01 7.56229980e-01 1.67839758e+00 3.72508168e+00
   8.26754857e+00 1.83492243e+01 4.07247722e+01 9.03856777e
   +01 2.00604455e+02 4.45227036e+02 9.88149108e+02
   2.19312526e+03
F2 = 2.73744922e-04 6.78046757e-04 4.74147028e-04
```

```
   5.29286482e-04 4.37554934e-04 7.79395953e-04 7.12961748e
   -04 1.02866063e-03 1.11030974e-03 1.42199361e-03
   1.64525016e-03 2.01784715e-03 2.39128685e-03 2.88882989e
   -03 3.44888565e-03 4.14225944e-03 4.95269649e-03
   5.92999994e-03 7.08369670e-03 8.45850112e-03 1.00802759e
   -02 1.19963355e-02 1.42424266e-02 1.68702720e-02
   1.99161929e-02 2.34310623e-02 2.74323411e-02 3.19535344e
   -02 3.69531084e-02 4.24137940e-02 4.81610368e-02
   5.40771459e-02 5.97403116e-02 6.48988052e-02 6.87597121e
   -02 7.10406441e-02 7.05594086e-02 6.75100382e-02
   6.05591237e-02 5.15334087e-02 3.91262616e-02 2.80884965e
   -02 1.57075729e-02 9.53756355e-03 2.26219168e-03
   1.89147343e-03

# Spectrum ID = 3
##KWW Relaxation Function with
##KWW_tau = 2.000000e+01, KWW_beta = 1.500000e-01
##and 48 prony terms in use
##Prony L2 Projection Error = 1.767624e-04
##
RELAX_TIME3 = 6.84998022e-19 2.33830085e-18 7.98199512e-18
   2.72472407e-17 9.30108469e-17 3.17500687e-16 1.08381645e
   -15 3.69970255e-15 1.26292593e-14 4.31110847e-14
   1.47163470e-13 5.02355418e-13 1.71483430e-12 5.85373733e
   -12 1.99822460e-11 6.82111499e-11 2.32844745e-10
   7.94835968e-10 2.71324232e-09 9.26189071e-09 3.16162766e
   -08 1.07924934e-07 3.68411232e-07 1.25760407e-06
   4.29294182e-06 1.46543336e-05 5.00238535e-05 1.70760813e
   -04 5.82907018e-04 1.98980425e-03 6.79237140e-03
   2.31863557e-02 7.91486597e-02 2.70180895e-01 9.22286190e
   -01 3.14830483e+00 1.07470148e+01 3.66858779e+01
   1.25230463e+02 4.27485173e+02 1.45925815e+03 4.98130572e
   +03 1.70041242e+04 5.80450698e+04 1.98141939e+05
   6.76374893e+05 2.30886504e+06 7.88151340e+06
F3 = 3.18457650e-04 1.86938527e-04 3.10489826e-04
   3.33676491e-04 4.21468277e-04 4.95118502e-04 6.01404460e
   -04 7.18830255e-04 8.65690264e-04 1.03855044e-03
   1.24791649e-03 1.49787231e-03 1.79815900e-03 2.15752484e
   -03 2.58796371e-03 3.10269763e-03 3.71782332e-03
   4.45187248e-03 5.32658985e-03 6.36699094e-03 7.60175031e
   -03 9.06325319e-03 1.07875231e-02 1.28137970e-02
   1.51834846e-02 1.79385468e-02 2.11183988e-02 2.47559774e
   -02 2.88706854e-02 3.34609029e-02 3.84902051e-02
   4.38766612e-02 4.94694209e-02 5.50425048e-02 6.02605683e
   -02 6.47068618e-02 6.78369714e-02 6.91207509e-02
```

```
      6.79495189e-02 6.40617228e-02 5.71802564e-02 4.80551299e
      -02 3.69798578e-02 2.63566562e-02 1.57948677e-02
      9.47733572e-03 2.83252334e-03 2.46653735e-03

   # Spectrum ID = 4
   ##KWW Relaxation Function with
   ##KWW_tau = 2.000000e+01, KWW_beta = 1.500000e-01
   ##and 48 prony terms in use
   ##Prony L2 Projection Error = 1.767624e-04
   ##
   RELAX_TIME4 = 6.84998022e-19 2.33830085e-18 7.98199512e-18
      2.72472407e-17 9.30108469e-17 3.17500687e-16 1.08381645e
      -15 3.69970255e-15 1.26292593e-14 4.31110847e-14
      1.47163470e-13 5.02355418e-13 1.71483430e-12 5.85373733e
      -12 1.99822460e-11 6.82111499e-11 2.32844745e-10
      7.94835968e-10 2.71324232e-09 9.26189071e-09 3.16162766e
      -08 1.07924934e-07 3.68411232e-07 1.25760407e-06
      4.29294182e-06 1.46543336e-05 5.00238535e-05 1.70760813e
      -04 5.82907018e-04 1.98980425e-03 6.79237140e-03
      2.31863557e-02 7.91486597e-02 2.70180895e-01 9.22286190e
      -01 3.14830483e+00 1.07470148e+01 3.66858779e+01
      1.25230463e+02 4.27485173e+02 1.45925815e+03 4.98130572e
      +03 1.70041242e+04 5.80450698e+04 1.98141939e+05
      6.76374893e+05 2.30886504e+06 7.88151340e+06
   F4 = 3.18457650e-04 1.86938527e-04 3.10489826e-04
      3.33676491e-04 4.21468277e-04 4.95118502e-04 6.01404460e
      -04 7.18830255e-04 8.65690264e-04 1.03855044e-03
      1.24791649e-03 1.49787231e-03 1.79815900e-03 2.15752484e
      -03 2.58796371e-03 3.10269763e-03 3.71782332e-03
      4.45187248e-03 5.32658985e-03 6.36699094e-03 7.60175031e
      -03 9.06325319e-03 1.07875231e-02 1.28137970e-02
      1.51834846e-02 1.79385468e-02 2.11183988e-02 2.47559774e
      -02 2.88706854e-02 3.34609029e-02 3.84902051e-02
      4.38766612e-02 4.94694209e-02 5.50425048e-02 6.02605683e
      -02 6.47068618e-02 6.78369714e-02 6.91207509e-02
      6.79495189e-02 6.40617228e-02 5.71802564e-02 4.80551299e
      -02 3.69798578e-02 2.63566562e-02 1.57948677e-02
      9.47733572e-03 2.83252334e-03 2.46653735e-03

end parameters for model spectacular

end property specification for material 828_dea_gmb
```

APPENDIX D. Sierra/SM material definition for 828/CTBN/DEA/GMB: Development SPECTACULAR calibration

```
# File: 828_ctbn_dea_gmb_sand2022-6360_table5-08_devel.txt
#
# WARNING: As of LAME 5.4, this calibration was produced using a
   model form
# that is not in the release version of SPECTACULAR. Check the
   current LAME
# documentation before deploying this calibration.
#
# Material: 828/CTBN/DEA/GMB
# Calibration: SAND2022-6360, Table 5-8 (development)
#
# 2022-02
# Ken Cundiff (kcundif@sandia.gov)
# Calibrated from data on Polymer Properties Database website
#
# NOTE: Set stress free-temperature based on application
#
# --- Material Information from Polymer Properties Database
   website ---
#
# 100 pbw adduct of digylcidyl ether of bisphenol A (Epon 828)
   and Hycar
#  1300x8 carboxyl terminated butadine acrylonitrile rubber (CTBN
   )
# 12 pbw diethanolamine
# 28 pbw 3M D32 glass microbaloons (48% by volume)
# Cured 24 hours at 71 C

begin material 828_ctbn_dea_gmb

   density = 770 # kg/m^3
   thermal log strain function = sierra_constant_function_zero

   begin parameters for model spectacular
      bulk modulus      = 3.1E9     # Pa
      shear modulus     = 1.089E9   # Pa
```

```
bulk glassy 0     = 3.1E9     # Pa
bulk glassy 1     = -3.3E6    # Pa/K
bulk rubbery 0    = 2.5E9     # Pa
bulk rubbery 1    = -3.5E6    # Pa/K
shear glassy 0    = 1.089E9   # Pa
shear glassy 1    = -9.2E6    # Pa/K
shear rubbery 0   = 20E6      # Pa
shear rubbery 1   = 0         # Pa/K
volcte glassy 0   = 144E-6    # K^-1
volcte glassy 1   = 0.5E-6    # K^-2
volcte rubbery 0  = 333E-6    # K^-1
volcte rubbery 1  = 0.8E-6    # K^-2
heat capacity glassy 0 = 1.156E6 # J/(m^3*K)
heat capacity glassy 1 = -1783 # J/(m^3*K^2)
heat capacity rubbery 0 = 1.410E6 # J/(m^3*K)
heat capacity rubbery 1 = -2270 # J/(m^3*K^2)
reference temperature = 338   # K
wlf c1            = 14.9      # None
wlf c2            = 53.4      # K
clock c1          = 0         # None
clock c2          = 0         # K
clock c3          = 1000      # K
clock c4          = 18200     # K
shift factor model = 4
stress free temperature = {stress_free_temperature} # K
# === NOT IMPLEMNTED OR UNDER DEVELOPMENT ===
bulk glassy 2     = 0
bulk rubbery 2    = 0
shear glassy 2    = 0
shear rubbery 2   = 0
volcte glassy 2   = 0
volcte rubbery 2  = 0
clock c5          = 0
clock c6          = 0
#Tmatch_wlf_arh    = -2929
#EACT_ON_R         = 60493.08479

#RELAX_TIMEi terms have units of s
#Fi terms are unitless

# Spectrum ID = 1
##KWW Relaxation Function with
##KWW_tau = 1.495817e+03, KWW_beta = 3.584686e-01
##and 27 prony terms in use
##Prony L2 Projection Error = 2.189357e-04
```

```
##
RELAX_TIME1 = 1.49918112e-05 8.21219994e-05 4.49847100e-04
   1.05285274e-03 2.46416813e-03 5.76730662e-03 1.34981965e
   -02 3.15920969e-02 7.39402914e-02 1.73054885e-01
   4.05029419e-01 9.47958389e-01 2.21866626e+00 5.19271737e
   +00 1.21533888e+01 2.84446174e+01 6.65737164e+01
   1.55813652e+02 3.64676865e+02 8.53514528e+02 1.99762343e
   +03 4.67537369e+03 1.09425625e+04 2.56107171e+04
   5.99410636e+04 1.40290141e+05 3.28344583e+05
F1 = 3.95435043e-04 1.32399805e-03 1.45912123e-03
   1.11424259e-03 1.94923860e-03 2.41922056e-03 3.39508759e
   -03 4.52309645e-03 6.15885296e-03 8.28649989e-03
   1.11887280e-02 1.50331186e-02 2.01599306e-02 2.68949421e
   -02 3.56656040e-02 4.68588991e-02 6.07723161e-02
   7.73095294e-02 9.55873439e-02 1.13180287e-01 1.25436599e
   -01 1.25386387e-01 1.06610298e-01 7.00638712e-02
   3.05916339e-02 6.88935142e-03 5.66289332e-04

# Spectrum ID = 2
##KWW Relaxation Function with
##KWW_tau = 6.946172e-01, KWW_beta = 1.919384e-01
##and 30 prony terms in use
##Prony L2 Projection Error = 1.222320e-03
##
RELAX_TIME2 = 1.63253383e-16 7.99062171e-16 3.91110030e-15
   1.91433234e-14 9.36991645e-14 4.58621173e-13 2.24477328e
   -12 1.09872971e-11 5.37785699e-11 2.63225301e-10
   1.28838605e-09 6.30615145e-09 3.08661725e-08 1.51077977e
   -07 7.39468271e-07 3.61941120e-06 1.77156181e-05
   8.67110992e-05 4.24417296e-04 2.07735853e-03 1.01678666e
   -02 4.97677746e-02 2.43594010e-01 1.19229847e+00
   5.83583991e+00 2.85641794e+01 1.39810611e+02 6.84318872e
   +02 3.34947623e+03 1.63943908e+04
F2 = 1.90342700e-05 5.29126359e-04 3.91278848e-04
   7.05610400e-04 8.66738677e-04 1.21985325e-03 1.62957378e
   -03 2.21795091e-03 2.99539529e-03 4.05264588e-03
   5.47127803e-03 7.37759811e-03 9.92546067e-03 1.33151325e
   -02 1.77914540e-02 2.36451333e-02 3.11944748e-02
   4.07438674e-02 5.24904380e-02 6.63636828e-02 8.17535017e
   -02 9.71715250e-02 1.09872796e-01 1.15894265e-01
   1.10789987e-01 9.22395188e-02 6.28614634e-02 3.24415595e
   -02 1.07697466e-02 2.38442661e-03

# Spectrum ID = 3
##KWW Relaxation Function with
```

```
##KWW_tau = 1.495817e+03, KWW_beta = 3.584686e-01
##and 27 prony terms in use
##Prony L2 Projection Error = 2.189357e-04
##
RELAX_TIME3 = 1.49918112e-05 8.21219994e-05 4.49847100e-04
   1.05285274e-03 2.46416813e-03 5.76730662e-03 1.34981965e
   -02 3.15920969e-02 7.39402914e-02 1.73054885e-01
   4.05029419e-01 9.47958389e-01 2.21866626e+00 5.19271737e
   +00 1.21533888e+01 2.84446174e+01 6.65737164e+01
   1.55813652e+02 3.64676865e+02 8.53514528e+02 1.99762343e
   +03 4.67537369e+03 1.09425625e+04 2.56107171e+04
   5.99410636e+04 1.40290141e+05 3.28344583e+05
F3 = 3.95435043e-04 1.32399805e-03 1.45912123e-03
   1.11424259e-03 1.94923860e-03 2.41922056e-03 3.39508759e
   -03 4.52309645e-03 6.15885296e-03 8.28649989e-03
   1.11887280e-02 1.50331186e-02 2.01599306e-02 2.68949421e
   -02 3.56656040e-02 4.68588991e-02 6.07723161e-02
   7.73095294e-02 9.55873439e-02 1.13180287e-01 1.25436599e
   -01 1.25386387e-01 1.06610298e-01 7.00638712e-02
   3.05916339e-02 6.88935142e-03 5.66289332e-04

# Spectrum ID = 4
##KWW Relaxation Function with
##KWW_tau = 9.983389e+01, KWW_beta = 2.836508e-01
##and 28 prony terms in use
##Prony L2 Projection Error = 1.836360e-04
##
RELAX_TIME4 = 8.07308941e-09 2.45708861e-08 7.47828261e-08
   2.27605593e-07 6.92729982e-07 2.10836132e-06 6.41691218e
   -06 1.95302207e-05 5.94412874e-05 1.80912786e-04
   5.50617891e-04 1.67583545e-03 5.10049621e-03 1.55236372e
   -02 4.72470330e-02 1.43798911e-01 4.37659794e-01
   1.33204135e+00 4.05414020e+00 1.23389959e+01 3.75544040e
   +01 1.14298868e+02 3.47874813e+02 1.05877588e+03
   3.22244191e+03 9.80767695e+03 2.98501974e+04 9.08506970e
   +04
F4 = 4.09711024e-04 5.43328981e-04 5.44175776e-04
   9.45840341e-04 1.15355578e-03 1.67129625e-03 2.23176098e
   -03 3.08828378e-03 4.20153738e-03 5.75114305e-03
   7.83535306e-03 1.06683595e-02 1.44749746e-02 1.95691547e
   -02 2.63078033e-02 3.51030960e-02 4.63379049e-02
   6.02609933e-02 7.66976946e-02 9.46706067e-02 1.11714060e
   -01 1.23448478e-01 1.23598436e-01 1.06797774e-01
   7.35575695e-02 3.60091311e-02 1.01846177e-02 1.40177598e
   -03
```

```
   end parameters for model spectacular

end material 828_ctbn_dea_gmb
```

APPENDIX E. Sierra/SM material definition for 828/DEA/GMB: Development SPECTACULAR calibration

```
# File: 828_dea_gmb_sand2022-6360_table5-08_devel.txt
#
# WARNING: As of LAME 5.4, this calibration was produced using a
   model form
# that is not in the release version of SPECTACULAR. Check the
   current LAME
# documentation before deploying this calibration.
#
# Material: 828/DEA/GMB
# Calibration: SAND2022-6360, Table 5-8 (development)
#
# 2022-02
# Ken Cundiff (kcundif@sandia.gov)
# Calibrated from data on Polymer Properties Database website
#
# NOTE: Set stress free-temperature based on application
#
# --- Material Information from Polymer Properties Database
   website ---
#
# 100 pbw adduct of digylcidyl ether of bisphenol A (Epon 828)
# 12 pbw diethanolamine
# 28 pbw 3M D32 glass microbaloons (48% by volume)
# Cured 24 hours at 71 C

begin material 828_dea_gmb

   density = 760 # kg/m^3
   thermal log strain function = sierra_constant_function_zero

   begin parameters for model spectacular
      bulk modulus      = 3.2E9     # Pa
      shear modulus     = 1.118E9   # Pa
      bulk glassy 0     = 3.2E9     # Pa
      bulk glassy 1     = -3.7E6    # Pa/K
      bulk rubbery 0    = 2.6E9     # Pa
```

```
bulk rubbery 1    = -3.9E6    # Pa/K
shear glassy 0    = 1.118E9   # Pa
shear glassy 1    = -2E6      # Pa/K
shear rubbery 0   = 40E6      # Pa
shear rubbery 1   = 0         # Pa/K
volcte glassy 0   = 115E-6    # K^-1
volcte glassy 1   = 0.4E-6    # K^-2
volcte rubbery 0  = 296E-6    # K^-1
volcte rubbery 1  = 0.1E-06   # K^-2
heat capacity glassy 0 = 1.122E6 # J/(m^3*K)
heat capacity glassy 1 = -2356 # J/(m^3*K^2)
heat capacity rubbery 0 = 1.509E6 # J/(m^3*K)
heat capacity rubbery 1 = -2459 # J/(m^3*K^2)
reference temperature = 348   # K
wlf c1            = 13.8      # None
wlf c2            = 53.9      # K
clock c1          = 0         # None
clock c2          = 0         # K
clock c3          = 1000      # K
clock c4          = 12900     # K
shift factor model = 4
stress free temperature = {stress_free_temperature} # K
# === NOT IMPLEMNTED OR UNDER DEVELOPMENT ===
bulk glassy 2     = 0
bulk rubbery 2    = 0
shear glassy 2    = 0
shear rubbery 2   = 0
volcte glassy 2   = 0
volcte rubbery 2  = 0
clock c5          = 0
clock c6          = 0

#RELAX_TIMEi terms have units of s
#Fi terms are unitless

# Spectrum ID = 1
##KWW Relaxation Function with
##KWW_tau = 2.555677e+01, KWW_beta = 4.223478e-01
##and 26 prony terms in use
##Prony L2 Projection Error = 2.654809e-04
##
RELAX_TIME1 = 4.26099189e-06 1.90017129e-05 8.47373338e-05
   1.78943454e-04 3.77882551e-04 7.97990756e-04 1.68515123e
   -03 3.55860598e-03 7.51486055e-03 1.58694527e-02
   3.35122024e-02 7.07691520e-02 1.49446247e-01 3.15592036e
```

```
   -01 6.66449209e-01 1.40736932e+00 2.97200202e+00
   6.27610387e+00 1.32535171e+01 2.79880194e+01 5.91034984e
   +01 1.24811387e+02 2.63569548e+02 5.56591095e+02
   1.17537724e+03 2.48209441e+03
F1 = 2.52814407e-04 1.47808681e-03 1.04755448e-03
   1.78149287e-03 1.28690083e-03 3.08491432e-03 3.06446601e
   -03 5.10493230e-03 6.30740523e-03 9.11034229e-03
   1.20858591e-02 1.67143048e-02 2.25359502e-02 3.06218995e
   -02 4.11094163e-02 5.48570896e-02 7.20427573e-02
   9.25418905e-02 1.14468626e-01 1.33100459e-01 1.39446913e
   -01 1.22374615e-01 7.93388319e-02 3.05378226e-02
   4.79955348e-03 1.58798039e-04

# Spectrum ID = 2 (shear)
##KWW Relaxation Function with
##KWW_tau = 6.612664e-01, KWW_beta = 2.529541e-01
##and 29 prony terms in use
##Prony L2 Projection Error = 2.389765e-04
##
RELAX_TIME2 = 3.05300475e-12 1.01877210e-11 3.39959052e-11
   1.13442601e-10 3.78552169e-10 1.26320927e-09 4.21526487e
   -09 1.40661238e-08 4.69379371e-08 1.56629501e-07
   5.22664651e-07 1.74410527e-06 5.81999027e-06 1.94210105e
   -05 6.48069209e-05 2.16257388e-04 7.21639867e-04
   2.40807541e-03 8.03562475e-03 2.68144697e-02 8.94785169e
   -02 2.98585245e-01 9.96363723e-01 3.32481490e+00
   1.10947376e+01 3.70225733e+01 1.23542438e+02 4.12254810e
   +02 1.37567326e+03
F2 = 4.62643796e-04 4.36947952e-04 6.09271260e-04
   8.47591092e-04 1.12860831e-03 1.54240300e-03 2.08083521e
   -03 2.82135316e-03 3.81332549e-03 5.15427037e-03
   6.95415598e-03 9.36685561e-03 1.25838808e-02 1.68477315e
   -02 2.24504120e-02 2.97224485e-02 3.90035131e-02
   5.05550128e-02 6.44264009e-02 8.01639255e-02 9.64758944e
   -02 1.10688806e-01 1.18668181e-01 1.15200027e-01
   9.69179484e-02 6.57737816e-02 3.27830960e-02 9.94133463e
   -03 1.74010061e-03

# Spectrum ID = 3
##KWW Relaxation Function with
##KWW_tau = 2.555677e+01, KWW_beta = 4.223478e-01
##and 26 prony terms in use
##Prony L2 Projection Error = 2.654809e-04
##
RELAX_TIME3 = 4.26099189e-06 1.90017129e-05 8.47373338e-05
```

```
      1.78943454e-04 3.77882551e-04 7.97990756e-04 1.68515123e
      -03 3.55860598e-03 7.51486055e-03 1.58694527e-02
      3.35122024e-02 7.07691520e-02 1.49446247e-01 3.15592036e
      -01 6.66449209e-01 1.40736932e+00 2.97200202e+00
      6.27610387e+00 1.32535171e+01 2.79880194e+01 5.91034984e
      +01 1.24811387e+02 2.63569548e+02 5.56591095e+02
      1.17537724e+03 2.48209441e+03
   F3 = 2.52814407e-04 1.47808681e-03 1.04755448e-03
      1.78149287e-03 1.28690083e-03 3.08491432e-03 3.06446601e
      -03 5.10493230e-03 6.30740523e-03 9.11034229e-03
      1.20858591e-02 1.67143048e-02 2.25359502e-02 3.06218995e
      -02 4.11094163e-02 5.48570896e-02 7.20427573e-02
      9.25418905e-02 1.14468626e-01 1.33100459e-01 1.39446913e
      -01 1.22374615e-01 7.93388319e-02 3.05378226e-02
      4.79955348e-03 1.58798039e-04

   # Spectrum ID = 4
   ##KWW Relaxation Function with
   ##KWW_tau = 3.031893e+01, KWW_beta = 2.527341e-01
   ##and 29 prony terms in use
   ##Prony L2 Projection Error = 2.400520e-04
   ##
   RELAX_TIME4 = 1.36835085e-10 4.57090920e-10 1.52688990e-09
      5.10050118e-09 1.70379752e-08 5.69145244e-08 1.90120190e
      -07 6.35087214e-07 2.12147783e-06 7.08669313e-06
      2.36727524e-05 7.90776739e-05 2.64155109e-04 8.82397246e
      -04 2.94760492e-03 9.84633035e-03 3.28911858e-02
      1.09871401e-01 3.67020050e-01 1.22601256e+00 4.09543510e
      +00 1.36806010e+01 4.56993798e+01 1.52656547e+02
      5.09941744e+02 1.70343550e+03 5.69024313e+03 1.90079794e
      +04 6.34952272e+04
   F4 = 4.63192636e-04 4.36324508e-04 6.10039151e-04
      8.47373114e-04 1.12913850e-03 1.54261284e-03 2.08142129e
      -03 2.82196250e-03 3.81424947e-03 5.15544377e-03
      6.95575376e-03 9.36894535e-03 1.25866268e-02 1.68512687e
      -02 2.24548918e-02 2.97279628e-02 3.90100244e-02
      5.05622320e-02 6.44335769e-02 8.01696927e-02 9.64781275e
      -02 1.10685074e-01 1.18656819e-01 1.15182418e-01
      9.68999958e-02 6.57635961e-02 3.27836723e-02 9.94549480e
      -03 1.74269761e-03

end parameters for model spectacular

end material 828_dea_gmb
```

DISTRIBUTION

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